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[Jour. Indian Chem. Soc., Vol. 36, No. 3, 1959]

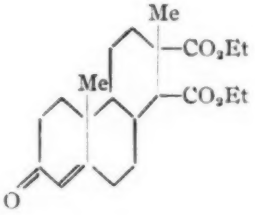
SYNTHESIS OF ALICYCLIC SYSTEMS RELATED TO STEROIDS. PART III

By Suvas C. Ray and Usha Ranjan Ghatak

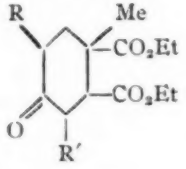
Synthesis of a few bicyclic and tricyclic intermediates in a projected synthesis of the characteristic tetracyclic system is described.

In a previous communication Dutta (this *Journal*, 1949, **26**, 109) reported a synthesis of tricyclic systems comprising B, C and D rings. The present investigation embodies the detailed study of a sequence of reactions leading to some useful intermediates for the synthesis of steroids.

It was originally in view to synthesise a hydroaromatic system of the following type*.



The two ester groups could be made to condense with ethyl acetate to build up the corresponding *cyclo*penta-1 : 3-dione or the β-propionic acid chain could be developed through *bis*-homologation of the secondary ester group for subsequent formation of the D-ring. The β-keto-ester (I), representing C-ring of the tetracyclic system, was expected to be an useful starting material for this purpose ; because the *cyclo*pentane ring could be easily fused after the desired perhydrophenanthrene nucleus had been successfully built up from the other side of the molecule. The keto-ester (I) could arise through cyclisation of the tetra-ester (Banerjee, this *Journal*, 1940, **17**, 427) leading to (I) and/or (II) (Mukherjee and Raha, *J. Org. Chem.*, 1954, **19**, 1381).



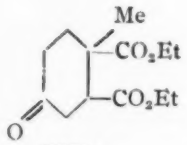
(I : R = H'; R' = CO_2Et).

(II : R = CO_2Et ; R' = H).

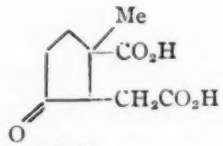
In view of recent observations in this laboratory (K. Sen, D.Phil. thesis, 1957, Calcutta University), the cyclised product (Mukherjee and Raha, *loc. cit.*) appears to be a

* The application of the Diels-Alder reaction with citraconic anhydride as the dienophile was at one time considered to be of much promise in synthesising this type of compounds (Dane *et al.*, *Annalen*, 1937, **532**, 29, 39 and subsequent papers), but later on found to be unrewarding because of the complexity of the products formed (Bachmann *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 1468 ; Singh, *ibid.*, 1956, **78**, 6109 ; Miescher *et al.*, *Helv. Chim. Acta*, 1949, **32**, 1572).

mixture of (I) and (II), although it has been characterised through the keto-diester (III).

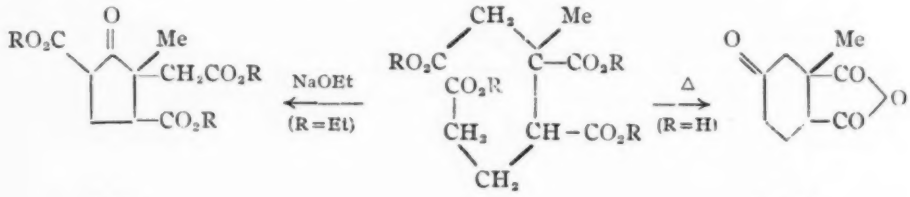


(III)



(IV)

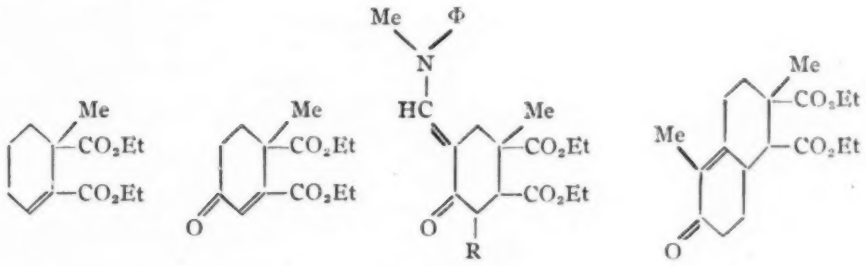
An attempt was made to utilise (III) with the expectation that the appropriate chain could be introduced at the hindered position (Banerjee *et al.*, *J. Amer. Chem. Soc.*, 1955, **77**, 408). The yield of (III) through (I) and (II) was not satisfactory. The tetra-acid corresponding to the above ester afforded (IV) on pyrolysis (Jeger *et al.*, *Helv. Chim. Acta*, 1954, **37**, 2297). It might be interesting to note here that with the isomeric tetra-acid (V), just the opposite results (VI, VIa) were obtained* (Stork and Dutta, unpublished work; cf. Dutta, this *Journal*, 1954, **31**, 875).



(VI) (V) (VIa)

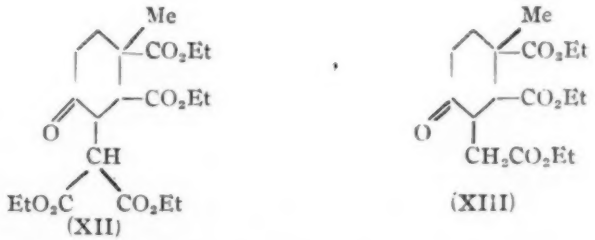
The unsaturated keto-ester (VIII) (Dutta, *Science & Culture*, 1943, **8**, 346) was employed for the present purpose. By oxidation of the ester (VII), obtained through the esterification of the corresponding acid (Linstead *et al.*, *J. Chem. Soc.*, 1936, 482) with selenium dioxide, (VIII) was obtained in a fairly good yield. It was then reduced with zinc dust and acetic acid, but the product failed to afford any ketonic derivative. So it was re-oxidised with chromic acid, and the keto-ester (III) afforded a yellow 2 : 4-dinitrophenylhydrazone in a quantitative yield. To determine the stereochemistry of the vicinal carboxyl groups, (III) was reduced and the dicarboxylic acid was found to be identical with *trans*-methyl*cyclo*hexane-1 : 2-dicarboxylic acid (Linstead *et al.*, *loc. cit.*). The keto-ester (III) was then condensed with ethyl formate, followed by reaction with methylaniline. The methylanilino compound (IX) was again condensed without further purification with ethyl formate to afford (X) and *in situ* with β-chloroethyl ethyl ketone. The crude condensation product was subjected to extensive acidic and alkaline hydrolysis. The desired bicyclic ester (XI) was isolated in a poor yield and characterised by ultraviolet absorption (λ_{alc}^{max} 249 mμ ; log ε 4.0) and a red 2 : 4-dinitrophenylhydrazone. Because of the poor yield at this step, it appeared futile to pursue further this line.

* Transformation of V → VI has been described by Banerjee and Das Gupta (*J. Amer. Chem. Soc.*, 1952, **74**, 1318).



(VII) (VIII) (IX: R=H) (X: R=CHO) (XI)

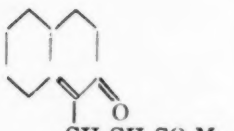
Again for the synthesis of (XI), the unsaturated keto-ester (VIII) was subjected to the Michael condensation with ethyl malonate. From theoretical considerations, it follows that the fragments of the addendum could take up two different positions in the *cyclo*hexane ring, leading to the formation of two isomeric products. From steric considerations, (XII) appeared to be more probable. The above condensation product was hydrolysed to afford a gummy material, which on esterification gave rise to the tri-ester (XIII). Partial hydrolysis of the same under controlled conditions furnished an acidic material, which failed to undergo the Arndt-Eistert homologation.



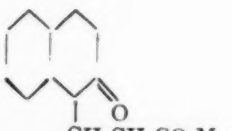
(XII) (XIII)

Methods, recently developed for the introduction of substituents at the α-position of an αβ-unsaturated carbonyl function (Conia, *Bull. soc. chim.*, 1954, 690, 943), have been utilised for the synthesis of (XVII). For this purpose, octalone (Robinson *et al.*, *J. Chem. Soc.*, 1937, 53) was prepared in a satisfactory yield by condensation with β-chloroethyl methyl ketone, in place of the Mannich base, and was condensed with methyl β-chloropropionate in presence of potassium butoxide[1] or better with potassium amylate[1] to afford (XIV). The condensation product exhibited a slight hypsochromic shift (λ_{max}^{alc} 242 mμ; log ε 3.97; Tishler *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 3816). It was then reduced catalytically to (XV) and the latter allowed to react with methylmagnesium iodide. The unsaturated acid (XVI) was subjected to ring-closure in presence of anhydrous zinc chloride in acetic acid-acetic anhydride (Bachmann *et al.*, *J. Org. Chem.*, 1948, **13**, 317), to afford the tricyclic ketone (XVII). From analytical values, the product appears to be a mixture of a lactone and (XVII). Further, this showed no absorption in the ultraviolet region, characterisitic of an αβ-unsaturated *cyclo*pentenone, and afforded a pale orange-yellow

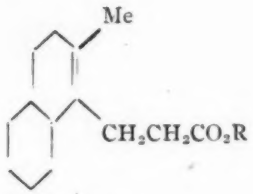
2 : 4-dinitrophenylhydrazone, suggesting also the absence of the above functional grouping. The ultraviolet absorption (λ_{max}^{alc} 366 mμ ; log ϵ 4.2) of this derivative lends an additional support to the above proposition. There is no convincing proof for assignment of the double bond to any particular position in the tricyclic system.



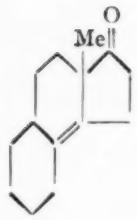
(XIV)



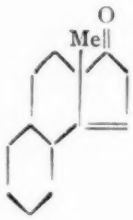
(XV)



(XVI : R = H)
(XVIA : R = Me)



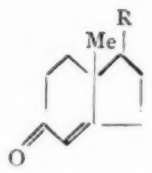
(XVII)



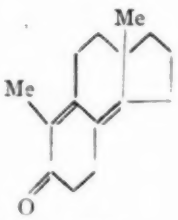
(XVIII)

Both the structures (XVII) or (XVIII) might appear equally probable, although (XVII) is more likely, as the double bond is more substituted. In the structure (XVIII), there would have been a tendency for the double bond to move in conjugation with the carbonyl group, specially during the formation of the dinitrophenylhydrazone. The products from ring-closure of (XVI) with polyphosphoric acid at different temperatures were complex in nature. At a lower temperature, most of the acid was converted into a lactonic product, and a small amount of a ketonic material could be isolated as an orange-red 2 : 4-dinitrophenylhydrazone, having the expected analytical values, whereas at the higher temperature a considerable quantity of a low-boiling fraction was obtained along with a higher boiling ketonic material, which gave a different 2 : 4-dinitrophenylhydrazone, bright red in colour. The lower boiling fraction corresponded closely to a hydrocarbon from elemental analysis (Frank *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 724). On dehydrogenation with palladium-charcoal, the product afforded an unstable red picrate. The higher boiling ketonic fraction was reduced with $LiAlH_4$ and the crude product was dehydrogenated to yield the same red picrate. Thorough search for the corresponding derivative of phenanthrene has failed, excluding thereby the possibility of the expansion of the five-membered ring (Frank *et al.*, *ibid.*, 1948, **70**, 1379).

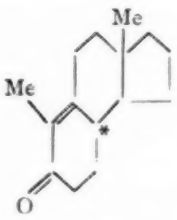
Next series of experiments is concerned with the synthesis of the following compounds.



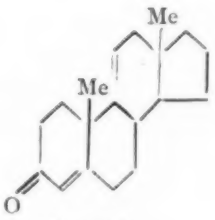
(XIX : R=H)
(XXVI : R=CO_2Me)



(XX)

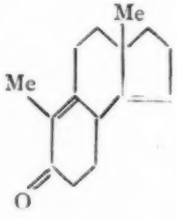


(XXI)

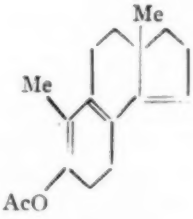


(XXII)

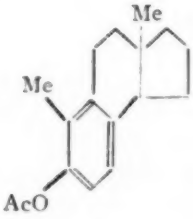
The bicyclic ketone (XIX) was synthesised in a much better yield through the condensation of β-chloroethyl methyl ketone with 2-methyl*cyclo*pentanone (Robinson *et al.*, *loc. cit.*). Attempts to condense β-chloroethyl ethyl ketone with (XIX) in presence of sodamide, potassium butoxide[t] or potassium amylate[t] failed to afford the desired product, but condensation took place readily in presence of sodium methoxide (Johnson *et al.*, *J. Amer. Chem. Soc.*, 1956, **78**, 6285), and the resulting crude product was subjected to ring-closure to afford (XX) along with a high-boiling residue, presumably a tetracyclic compound (Johnson, *loc. cit.*). Next it was planned to shift the γδ-double bond to the five-membered ring, leading to (XXIII), with the idea of condensing β-chloroethyl methyl ketone to the latter (Cooley *et al.*, *J. Chem. Soc.*, 1955, 2998) leading to a tetracyclic compound.



(XXIII)



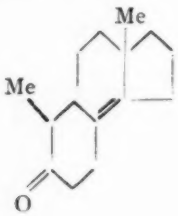
(XXIV)



(XXV)

The dienone (XX) was treated with acetyl chloride and acetic anhydride with a view to isolating (XXIV). The resulting product was found to be a mixture, boiling over a wide range. The higher boiling fraction showed no absorption in the ultraviolet region, characteristic of (XXIV). Moreover, a red 2 : 4-dinitrophenylhydrazone separated out slowly, which resinified on standing and could not be purified for further characterisation. The possibility of the formation of a phenolic material (XXV) was excluded, as the product, on mild alkaline hydrolysis, was insoluble in alkali and showed no ferric chloride reaction. As the dienone (XX) failed to condense with β-chloroethyl methyl ketone in presence of potassium butoxide[t] or amylate[t] (Coolie *et al.*, *loc. cit.*) to afford the tetracyclic compound, it was reduced with sodium and alcohol and the crude reduction product was oxidised with chromic acid. The ketonic material analysed for a mono-unsaturated ketone. It afforded a yellow 2 : 4-dinitrophenylhydrazone, which rapidly turned red. The ketone had no absorption in the ultraviolet, characteristic of αβ-unsaturated ketones. It also failed

to condense with β-chloroethyl methyl ketone in presence of sodium methoxide or potassium butoxide[6]. From these considerations, it appeared probable that the ketone might have the following structure :

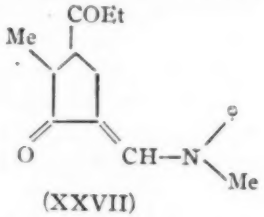


because the migration of "8 : 14"-double bond in steroids under acidic conditions is an established phenomenon.

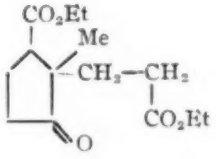
The dienone (XX) was reduced catalytically in presence of Pd-C in alcoholic solution. After absorption of one mole of hydrogen, the product was worked up. The reduced ketone, so obtained, has the desired ultraviolet absorption (λ^{alc}_{max} 255 mμ ; log ε 4.0) having a significant bathochromic shift. Evidently γδ-double bond has been reduced (cf. Shepherd *et al.*, *J. Amer. Chem. Soc.*, 1955, **77**, 1212 ; Wieland *et al.*, *Helv. Chim. Acta*, 1953, **36**, 646). Attempts to purify the red 2 : 4-dinitrophenylhydrazone revealed that the ketone (XXI) was a mixture of different stereoisomers, arising probably from non-stereospecific reduction of the γδ-double bond, although the decalone ring juncture (*) in (XXI), because of the presence of a vinylogous system, would probably equilibrate under acidic or alkaline conditions. With a view to reducing both the double bonds in the ketone (XX), it was hydrogenated in presence of the same catalyst till two moles of hydrogen were absorbed. The product on distillation afforded a series of fractions, boiling over a wide range. The lower boiling fractions corresponded closely to that of a hydrocarbon, as shown from elemental analyses. Absence of any appreciable amount of a ketonic material was also revealed in the infra-red studies. The highest boiling fraction afforded a yellow 2 : 4-dinitrophenylhydrazone, but the derivative was again found to be a complex mixture.

Experiments were also carried out simultaneously to synthesise (XXVI), so that the carbomethoxyl group might eventually serve the purpose of developing the characteristic C_{17}-side chain. The methylanilino compound (XXVII ; Dutta, this *Journal*, 1954, **31**, 875) failed to afford the desired bicyclic compound on condensation with β-chloroethyl methyl ketone in the presence of sodamide or potassium butoxide[6]. An attempt was made to condense the keto-diester (XXVIII) (Dutta, *loc. cit.*) with ethyl bromoacetate in presence of zinc, followed by alkaline hydrolysis and esterfication (Simonsen *et al.*, *J. Chem. Soc.*, 1937, 1576 ; Banerjee *et al.*, *J. Amer. Chem. Soc.*, 1955, **77**, 408 ; Heard *et al.*, *Canad. J. Chem.*, 1958, **36**, 1260), but failed to furnish the desired product. The keto-diester (XXVIII) was next subjected to partial hydrolysis (Brossi *et al.*, *Helv. Chim. Acta*, 1951, **34**, 244) and the half-ester was converted into the acid-chloride, and the

latter in the crude state was condensed with ethyl magnesiomalonate. During hydrolysis the product underwent ring-closure and the desired keto-ester (XXVI) was obtained on esterification.



(XXVII)



(XXVIII)

It exhibited the expected ultraviolet absorption (λ_{max}^{alc} 236 mμ ; log ε 3.9) and afforded a red 2 : 4-dinitrophenylhydrazone. It may be mentioned that the carbomethoxyl group is in the desired stereochemical configuration with respect to the angular methyl group (Dutta, *loc. cit.*).

Experimental

Ethyl Methyl-Δ^2*-cyclohexene-1 : 2-dicarboxylate* (VII).—A mixture of methyl-Δ^2-*cyclo*hexene-1 : 2-dicarboxylic acid (76 g), absolute ethyl alcohol (350 c.c.) and H_2SO_4 (conc., 40 c.c.) was refluxed gently for 30 hours in an oil-bath. Alcohol was removed to some extent under suction. The residue was poured on ice and extracted with benzene ; the extract was washed successively with water, sodium carbonate solution and water. On distillation, it afforded the di-ester, b.p. 132°/6 mm, yield 72 g. (Found : C, 65.4 ; H, 8.2. $C_{13}H_{20}O_4$ requires C, 65.0 ; H, 8.3%).

Ethyl Methyl-Δ^2*-cyclohexen-4-one-1 : 2-dicarboxylate* (VIII).—To the above ester (20 g.), dissolved in glacial acetic acid (35 c.c.), selenium dioxide (10 g.) was added and the mixture heated in an oil-bath at 125-30° for 2 hours, at 130-35° for 2 hours and finally at 135-40° for 2 hours (not to exceed 145°) with occasional swirling of the flask. The cooled solution was filtered through glass wool and the black selenium was washed with ether. The ethereal solution was washed repeatedly with sodium carbonate solution till free of acid and finally with water. The ether was removed and the residue distilled. The keto-ester passed over at 162-67°/6 mm, yield 17 g. (λ_{max}^{alc} 379 ; log ε 4.5). (Found : C, 61.7 ; H, 7.2. $C_{13}H_{18}O_5$ requires C, 61.4 ; H, 7.08%).

The 2 : 4-*dinitrophenylhydrazone* was crystallised from ethyl acetate-ethyl alcohol (2 : 1) in pale orange flakes, m.p. 169°. (Found : C, 52.82 ; H, 5.24 ; N, 12.65. $C_{19}H_{22}O_8N_4$ requires C, 52.53 ; H, 5.07 ; N, 12.90%).

Ethyl Methylcyclohexan-4-one-1 : 2-dicarboxylate (III).—The above keto-diester (12 g.) was dissolved in glacial acetic acid (100 c.c.) in a flask, fitted with a reflux condenser and a calcium chloride guard tube. Zinc dust (30.2 g.) was added in small amounts and thoroughly shaken. The flask was heated in an oil-bath and refluxed for 9 hours. While hot, the contents were poured in a large beaker, cooled and ether added. The mixture was filtered through glass wool. The ether-glacial acetic acid solution was successively washed with water, sodium carbonate solution and

water. It was dried over anhydrous sodium sulphate and the ether removed. The residue was distilled in vacuum, b.p. 155-62°/6 mm, yield 11 g. A solution of the above mentioned zinc-acetic acid reduced product (88 g.) in glacial acetic acid (100 c.c.) and benzene (100 c.c.) was dropped slowly into a solution of potassium dichromate (30 g.) in glacial acetic acid (300 c.c.), and allowed to stand with occasional shaking for 48 hours and then poured into water ; the benzene layer was separated and the aqueous layer was extracted with ether. The organic extract was washed successively with water, sodium bicarbonate solution and water. It was dried (sodium sulphate), the solvent removed and the residue was distilled, when the keto-ester was obtained as a clear colorless liquid, b.p. 136-40°/0.6 mm, yield 67.8 g.

The yellow 2 : 4-*dinitrophenylhydrazone* was crystallised from ethyl acetate in fine needles, m.p. 158°. (Found : C, 52.36 ; H, 5.36 ; N, 12.98. $C_{19}H_{24}O_8N_4$ requires C, 52.29 ; H, 5.50 ; N, 12.84%).

trans-*Methylcyclohexane*-1 : 2-*dicarboxylic Acid*.—The keto-diester (III, 2 g.) was refluxed for 20 hours with HCl (conc., 50 c.c.) and amalgamated zinc (25 g.). The reduced acid was extracted with ether, the solvent removed and the residue crystallised from dilute HCl, m.p. 212° (lit. 211-13°), alone or mixed with an authentic sample.

Ethyl 2 : 5-*Dimethyl*-6-*keto*-$\Delta^{5:10}$-*octahydronaphthalene*-1 : 2-*dicarboxylate* (XI).—Sodium dust (7.2 g.) was taken under dry benzene (200 c.c.), cooled, and absolute ethyl alcohol (20 c.c.) was added to it and left overnight. With further cooling, a mixture of the keto-dicarboxylic ester (III, 40 g.) and freshly distilled ethyl formate (36 g.) was added slowly with shaking, left overnight and then diluted with water. The benzene layer was washed with a 2% NaOH solution. The combined aqueous layer was slowly acidified with cold dilute HCl ; the liberated oil was taken up in ether and dried over sodium sulphate. The ether was removed and the residue dried in vacuum. The formylated product was dissolved in methyl alcohol (200 c.c.) and freshly distilled methylaniline (16 8 g.) added to it and left overnight. The methyl alcohol was removed and benzene (100 c.c.) added and removed under suction. The residue was dried on a steam-bath under reduced pressure (20 mm) for 1 hour. Sodium ethoxide, prepared from sodium (7.2 g.) and ethanol (18 c.c.), was covered with dry benzene (200 c.c.) and to this, after cooling in ice, was added slowly ethyl formate (36 g.), followed after 5 minutes by the benzene solution of the monomethylanilinomethylene compound and left overnight. The freshly distilled ethyl β-chloroethyl ketone (36 g.) was added after thorough cooling in ice. The whole was left overnight and then refluxed for 4 hours on a steam-bath. It was poured into HCl (conc., 40 c.c.) and water (150 c.c.). The aqueous layer was extracted with benzene and the extract was washed with water and the benzene removed. The residue was heated with HCl (conc., 40 c.c.) and water (65 c.c.) on the steam-bath for 1 hour. It was cooled and to this was added slowly a solution of NaOH (60 g.) in water (140 c.c.) and allowed to stand overnight in an atmosphere of nitrogen. It was finally refluxed for 2 hours at 110° (oil-bath), cooled and poured into HCl (conc., 140 c.c.) and crushed ice. It was extracted well with ether in which most of the gummy material remained undissolved. The extract was washed with water and dried over anhydrous sodium sulphate. The ether was removed and the residue dried well in vacuum and esterified with ethyl alcohol (300 c.c.) and H_2SO_4

(conc., 20 c.c.) for 28 hours. Almost half of the alcohol was removed under suction, cooled and poured on ice-chips. It was again extracted with ether after saturation with common salt. The extract was washed with sodium carbonate solution and water. The sodium carbonate extract was acidified and then extracted with ether and the residue on removal of the ether was re-esterified as before. The neutral products were taken together and finally distilled.

A mixture of products was obtained along with a major quantity of a polymeric product. The distillable residue (*ca.* 8 g.) was refractionated as follows: (*i*) 4.1 g., b.p. 130-40°/0.5 mm. (*ii*) 0.77 g., b. p. 155-65°/0.5 mm. (*iii*) 1.2 g., b.p. 170-80°/0.5 mm.

Fraction (*i*) corresponded to the monocyclic unchanged keto-ester (III). The middle fraction was further purified by evaporative distillation (150-60°/0.4 mm) and was collected as a viscous mass. It afforded a bright red 2:4-*dinitrophenylhydrazone*, which was crystallised from ethyl acetate-ethyl alcohol (2:1) in fine needles, m.p. 210°. (Found: C, 57.15; H, 5.74. $C_{24}H_{30}O_8N_4$ requires C, 57.37; H, 5.97%).

The last fraction also contained an appreciable amount of the desired bicyclic compound, as was evident through the formation of the dinitrophenylhydrazone.

Ethyl (1:2-*Dicarbethoxy*-4-*ketomethyl*cyclo*hexyl*)-3-*malonate* (XII) *and/or*-2-*malonate*. —To sodium (1.2 g.), dissolved in ethyl alcohol (20 c.c.), was added ethyl malonate (15 g., 1.5 *M*) and the mixture was cooled in a freezing mixture, and to it was added the unsaturated keto-diester (XV, 15 g.), dissolved in alcohol (10 c.c.). The colour of the solution gradually turned brown and it was allowed to stand for 3 days at room temperature. It was then poured over ice and HCl (dilute). The heavy oil, so obtained, was extracted with ether. The extract was repeatedly washed with water and dried. After removal of the solvent the residue was distilled, when the tetra-ester (10 g.) passed over at 210-15°/4 mm. (Found: C, 58.4; H, 6.9. $C_{20}H_{30}O_9$ requires C, 58.0; H, 7.2%).

Ethyl (1:2-*Dicarbethoxy*-4-*ketomethyl*cyclo*hexyl*)-3-*acetate* (XIII) *and/or*-2-*acetate*. —The above condensation product (30 g.) was hydrolysed by refluxing with an excess of HCl (conc.) for 24 hours, affording a clear solution. It was evaporated on the water-bath and then kept in a vacuum desiccator over solid KOH to remove most of the HCl. The gummy residue (20 g.) was thoroughly dried in vacuum and esterified by refluxing for 36 hours on the water-bath with a mixture of EtOH-H_2SO_4 (10:1). On working up in the usual way, the ethereal extract was washed with sodium carbonate solution, dried and distilled. The acidic fraction was re-esterified and the combined neutral fraction afforded a thick viscous oil (16 g.) boiling at 175-80°/3 mm. (Found: C, 59.6; H, 7.1. $C_{17}H_{26}O_7$ requires C, 59.6; H, 7.5%).

1-(*β*-*Carbomethoxyethyl*)-$\Delta^{1:9}$-*octalin*-2-*one* (XIV).—(*i*). Potassium butoxide[t], prepared from potassium (3.9 g.) and dry BuOH[t] (100 c.c.), was cooled in ice in an atmosphere of nitrogen and $\Delta^{1:9}$-octalin-2-one (13.5 g.) added slowly with shaking, and allowed to stand for half-an-hour. It was refluxed for 1 hour over a water-bath and then cooled in a freezing mixture. Methyl *β*-chloropropionate (11 g.) was added dropwise under nitrogen atmosphere, and the reaction mixture was allowed to stand overnight. Next day it was refluxed for 3 hours in an oil-bath at 120°, cooled, poured into

ice-water containing a little HCl and finally extracted with ether. On drying over sodium sulphate, the solvent was removed and the residue distilled. A lower boiling fraction (2.8 g.) below 130°/8 mm was collected, followed by another product (5 g.), b.p. 182-90°/7 mm. There was a considerable high boiling residue in the flask.

(*ii*). The above reaction was repeated using potassium (4.3 g.), dissolved in BuOH^t (100 c.c.). The excess alcohol was removed under diminished pressure. The potassium butoxide^t was then suspended in dry benzene (100 c.c.) and the condensation was carried out as before. Fraction (i) 4.2 g., 120-40°/8 mm. Fraction (ii) 4 g. 188°/8 mm.

(*iii*). The experiment was then repeated with potassium (10.1 g.), dissolved in amyl^t alcohol (300 c.c.). Excess alcohol was removed as usual and the amylate was taken in dry benzene (500 c.c.) and cooled in ice. The unsaturated ketone (35 g.) was added and condensed with methyl β-chloropropionate (32 g.), as described before. Fraction (i) 8.4 g., 120-40°/6 mm. Fraction (ii) 15.8 g., 184-88°/8 mm. The second fraction gave the following analytical data. (Found: C, 71.3; H, 8.67. $C_{14}H_{20}O_3$ requires C, 71.18; H, 8.47%).

1-(*β-Carbomethoxyethyl*)-*decalin*-2-*one* (XV).—The above unsaturated ketone (XIV, 2.37 g.) was hydrogenated with Pd-C (0.2 g., 10%) in alcohol (20 c.c.). Within 4 hours the theoretical amount of hydrogen was absorbed. The solution was filtered and distilled, b.p. 174-76°/8 mm, yield 2.2 g. (Found: C, 70.49; H, 9.23. $C_{14}H_{22}O_3$ requires C, 70.59; H, 9.24%).

β-Carboxyethyl-2-*methyl*-Δ^1-*octalin* (XVI).—Methylmagnesium iodide, prepared from magnesium (0.7 g.) and MeI (2.5 c.c.), was added with vigorous stirring to a solution of the keto-ester (XV, 5.5 g.) in ether (15 c.c.), cooled in a freezing mixture. The mixture was allowed to stand for 1 hour in the ice-bath temperature and for half-an-hour at room temperature. The product was decomposed with ice and H_2SO_4 (dil.) and extracted with ether. On removal of the solvent and the low-boiling products, the residue was taken in a Claisen flask, a tiny crystal of iodine was added and distilled slowly in vacuum, b.p. 130-60°/5 mm, yield 5.1 g. This was further heated with freshly fused potassium bisulphate (15 g.) at 130-40° for 1½ hours in an atmosphere of nitrogen. The product was decomposed with water and extracted with ether. On distillation the desired product (2.5 g.) passed over at 132-35°/0.3 mm along with a product (1 g.) boiling at 165-75°/0.4 mm; a non-distillable residue (*ca.* 1 g.) remained in the flask. The first fraction (2.5 g.) was hydrolysed by refluxing with a solution of KOH (3 g.) in MeOH (15 c.c.) and water (16 c.c.) for 2 hours. Next, the methanol was removed under suction over a warm water-bath, the residue diluted with water and the neutral material removed with ether. The aqueous portion was acidified and extracted again with ether after saturation with sodium chloride. The ethereal solution on evaporation left a gummy mass (1.8 g.), b.p. 147-49°/0.4 mm. (Found: C, 75.39; H, 9.56. $C_{14}H_{22}O_2$ requires C, 75.69; H, 9.9%).

A portion of it was esterified with an ethereal solution of diazomethane and the desired ester boiled at 130-32°/0.3 mm. (Found: C, 75.8; H, 9.7. $C_{15}H_{24}O_2$ requires C, 76.2; H, 10.1%).

1 : 2-(cyclo*Pentan-3'-one*)-2-*methyl*-$\Delta^{1:9}$-*octalin* (XVII).—The dried gummy acid (4 g.), obtained above, was dissolved in acetic anhydride (40 c.c.) and to this was added freshly fused powdered zinc chloride (0.7 g.), dissolved in glacial acetic acid (10 c.c.), and left at room temperature for 72 hours. The reaction mixture was heated for ½ hour on a boiling water-bath, cooled and taken in ether (200 c.c.) and the ethereal solution was washed with an ice-cold 5% NaOH solution until free of acid. It was washed with water, dried over anhydrous sodium sulphate and finally distilled, b.p. 132-35°/0.4 mm, yield 1.7 g. Much tarry material (*ca.* 2 g.) remained in the flask.

It afforded a 2 : 4-*dinitrophenylhydrazone* which crystallised from ethyl acetate-ethanol (1 : 1) in silky orange-yellow needles, m.p. 208.5°. (Found : C, 62.33 ; H, 6.48 ; N, 14.46. $C_{20}H_{24}O_4N_4$ requires C, 62.5 ; H, 6.25 ; N, 14.58%).

Ring-closure with Polyphosphoric Acid.—(*i*). The acid (XVI, 5 g.) was heated at 80° for 1 hour and at 110° for 2 hours with P.P.A. (P_2O_5, 10 g. and H_3PO_4, 6 c.c.). The reaction mixture was cooled and poured in water and extracted with ether. The ethereal extract was washed with a 10% NaOH solution, water and finally dried. After removal of the solvent the residue was distilled. Two fractions were collected : Fraction (i) 1.5 g., b.p. 105-107°/2 mm and fraction (ii) 0.6 g., b.p. 135-45°/0.4 mm. The second fraction gave a bright red 2:4-*dinitrophenylhydrazone*, crystallised from ethyl acetate-ethyl alcohol in small needles, m.p. 196° ($\lambda_{max}^{CHCl_3}$ 390 mμ ; log ε 4.4). (Found : C, 62.38 ; H, 6.33 ; N, 14.38. $C_{20}H_{24}O_4N_4$ requires C, 62.5 ; H, 6.25 ; N, 14.58%).

The first fraction (0.38 g.) was heated with Pd-C (0.09 g., 10%) at 300° for 4 hours. The product was taken up in benzene and finally distilled. It afforded a yellow liquid (0.25 g.), b.p. 110-20°/5 mm (bath temperature). It furnished an unstable picrate which crystallised from ethyl alcohol in long, red needles, m.p. 120-23° (the red needle-shaped picrate of 3-benz-indene melts at 125-27° ; Koelsch *et al.*, *J. Amer. Chem. Soc.*, 1943, **65**, 2313).

(*ii*). The experiment was repeated under identical conditions, but the reaction temperature was maintained at 90°. The acid (2 g.) afforded a liquid (0.95 g.) boiling at 132-37°/0.3 mm. It gave a 2:4-*dinitrophenylhydrazone* which crystallised in orange-red flakes from ethyl alcohol, m.p. 264° (decomp.). (Found : C, 62.5 ; H, 6.06 ; N, 14.6. $C_{20}H_{24}O_4N_4$ requires C, 62.5 ; H, 6.25 ; N, 14.58%).

5-*Keto*-8-*methyl*-$\Delta^{4:9}$-*tetrahydrohydrindene* (XIX).—Sodamide was prepared from sodium (24 g.) and liquid ammonia (*ca.* 700 c.c.) in presence of a small amount of ferric nitrate in a three-necked round-bottomed flask (2 litre) fitted with a stirrer and was protected from moisture by two KOH guard-tubes. After complete evaporation of ammonia the flask was rapidly fitted with a reflux condenser and sodamide was covered with dry ether (1200 c.c.). 2-Methyl*cyclo*pentanone (98 g.) was added slowly with stirring, when a brisk evolution of ammonia took place. The mixture was refluxed for 2 hours and then about one-fourth (*ca.* 300 c.c.) of ether was distilled off. The slightly yellowish white reaction mixture was cooled in a freezing mixture and freshly distilled β-chloro-

ethyl methyl ketone (113 g.) was added dropwise with vigorous stirring. It was left as such for ½ hour. The mixture was then refluxed for 2 hours with stirring. The volume was reduced and left overnight. After decomposition with ice-cold HCl (dil.), the ethereal layer was separated and the aqueous layer extracted with ether. The combined ethereal extract was washed with water and dried (Na_2SO_4). The solvent was distilled off and the residue furnished the first fraction, consisting of unchanged 2-methyl*cyclo*pentanone (*ca.* 20 g.) along with methylvinyl ketone and the condensation product (45 g.), b.p. 115-35°/7 mm. A considerable amount of a high-boiling product remained in the distillation flask. The ketone readily furnished an orange dinitrophenylhydrazone, which on crystallisation from ethyl acetate afforded the yellow derivative, m.p. 203°, of the uncyclised diketone (McQuillin *et al.*, *J. Chem. Soc.*, 1938, 1097, report m.p. 201°), and a scarlet-red dinitrophenylhydrazone of the desired bicyclic ketone, m.p. 153° (undepressed when mixed with the sample described below).

The above crude product (45 g.) was refluxed with KOH (47 g.) in methanol (950 c.c.) for 10 hours in an atmosphere of nitrogen. It was neutralised with acetic acid and the MeOH thoroughly removed on a boiling water-bath. It was diluted with water and extracted twice with ether. The ethereal solution was washed successively with water, 5% Na_2CO_3 solution, water and 0.5% HCl solution, and dried (Na_2SO_4). After removal of the solvent, the desired ketone distilled as a sweet-smelling colorless liquid (26 g.), b.p. 105°/2-3 mm, λ_{max}^{alc} 238 mμ (log ε 4.05). A high-boiling product remained in the distillation flask. A scarlet-red 2 : 4-*dinitrophenylhydrazone*, m.p. 153-54° (lit. m.p. 153°) was obtained in a quantitative yield. The *semicarbazone* was crystallised from dilute ethanol in white needles, m.p. 204-205° (lit. m.p. 205°).

1 : 6-*Dimethyl*-2-*keto*-5 : 6-cyclo*pentano*-2 : 3 : 4 : 6 : 7 : 8-*hexahydronaphthalene* (XX).—To a stirred solution of sodium methoxide, prepared from Na (13.6 g.) and dry MeOH (400 c.c.), a solution of the above bicyclic ketone (42 g.) in methanol (50 c.c.) was added in one lot under an atmosphere of nitrogen. The reaction mixture was placed in an ice-bath and a solution of β-chloroethyl ethyl ketone (35 g.) in methanol (100 c.c.) was added during 1½ hours with vigorous stirring. Stirring was continued for another 2 hours. After refluxing for another hour, the reaction mixture was decomposed with ice-cold 2*N*-H_2SO_4 and extracted repeatedly with ether after saturation with sodium chloride. The ethereal extract was washed with water and dried with sodium sulphate. After removal of the solvent, the residue was fractionated, affording some recovered hydrindone (*ca.* 10 g.), a slightly coloured product (25.2 g.), b.p. 130-40°/0.2 mm and a thick yellow liquid (10.7 g.), b.p. 180-95°/0.3 mm. The middle fraction (b.p. 130-40°/0.2 mm, 25.2 g.) was refluxed for 4 hours with a solution of sodium methoxide from Na (4 g.) and dry MeOH (600 c.c.) under an atmosphere of nitrogen. The reaction mixture was cooled and acidified with glacial acetic acid. After removal of the methanol on a water-bath, the residue was diluted with water and extracted with ether thrice. The ethereal extract was washed successively with water, 5% Na_2CO_3 solution and water till neutral. After removal of the solvent from the dried extract, the residue on distillation yielded a light yellowish liquid (21.2 g.), b.p. 125-28°/0.2 mm, with a small amount

of a high-boiling product, which remained in the distillation flask ; λ_{max}^{alc} 315 mμ (log ε 3.95). (Found : C, 82.91 ; H, 9.18. $C_{15}H_{20}O$ requires C, 83.33 ; H, 9.26%).

The 2 : 4-*dinitrophenylhydrazone*, after three recrystallisations from ethyl acetate-alcohol mixture, furnished chocolate-red microneedles, m.p. 201-202°. (Found : C, 63.85 ; H, 5.90. $C_{21}H_{24}O_4N_4$ requires C, 63.63 ; H, 6.06%).

Methyl 5-Keto-8-methyl-$\Delta^{4:9}$*-tetrahydrohydrindene-carboxylate* (XXVI).—A cold solution of the diester (XXVIII, 10 g.) in ethanol (30 c.c.) was mixed with an ice-cold ethanolic KOH solution (60 c.c., 0.6 *N*). After allowing it to stand overnight at room temperature, the mixture was heated just to boiling and diluted with ice-cold water. After saturation with sodium chloride, the solution was extracted twice with ether. On removal of the solvent, a small amount of a neutral product (*ca.* 0.8 g.) was left behind. The aqueous layer was cooled, acidified with HCl (1 : 1) and thoroughly extracted with ether. The ethereal extract was washed with water and dried over sodium sulphate. After removal of the solvent, the residue was dried in vacuum, when an almost colorless gummy mass (*ca.* 7.5 g.) remained. [Found : Equiv., 232.8 ; monobasic acid ($C_{12}H_{18}O_5$) requires equiv. 242 ; dibasic acid ($C_{10}H_{14}O_5$) requires equiv. 107%].

To a well-stirred cooled solution of the above half-ester (*ca.* 7 g.) in dry ether (25 c.c.) and pyridine (2.3 g.) pure thionyl chloride (2.2 c.c.) was added dropwise and the mixture was kept as such for half-an-hour when pyridine hydrochloride separated out. After keeping for another 30 minutes at room temperature, the ethereal layer was filtered off through glass wool and the solution was directly used in the next step.

Ethyl magnesiomalonate was prepared by adding a solution of redistilled ethyl malonate (10.6 g.) in dry ethanol (6 c.c.) to a stirred suspension of magnesium (1.7 g.) in dry ether (50 c.c.), absolute ethanol (1.7 c.c.) and dry CCl_4 (0.1 c.c.). The mixture was refluxed until whole of the magnesium dissolved (about 3 hours). To the ice-cold mixture the ethereal solution of the above chloride was added dropwise with vigorous stirring, left as such for 15 minutes and then refluxed for 45 minutes. The reaction mixture was decomposed with ice-cold 2*N*-H_2SO_4. The ethereal layer was separated, washed with H_2SO_4 (dil.), then with sodium bicarbonate solution (2%) and finally with water. After drying over sodium sulphate, the ether was distilled off, yielding a thick, red, oily product. This gave a pink colour with ferric chloride solution. The crude product was mixed with acetic acid (78 c.c.), H_2SO_4 (10 c.c.) and water (52 c.c.) and then slowly refluxed for 7 hours. The acetic acid was removed by passing steam. The reaction mixture was cooled and treated with NaOH (25 g.) in water (400 c.c.) and heated on the water-bath for 7 hours. The reaction mixture was cooled and acidified with excess of ice-cold HCl (conc.) (Congo red) and extracted with ether after saturation with sodium chloride. The ethereal extract was dried with sodium sulphate and the solvent removed. The residual gummy mass (*ca.* 5 g.) after drying in vacuum was directly esterified by refluxing for 16 hours with MeOH-H_2SO_4 (absolute, 100 c.c. and 10 c.c., conc.). After dilution with water and saturation with sodium chloride the separated oily product was worked up in the usual manner. The residue, after removal

of the solvent yielded on distillation a slightly yellowish liquid (3 g.) having a smell of sulphur impurities; b.p. 120-25°/0.15 mm. The compound readily formed an orange-red 2:4-*dinitrophenylhydrazone* in 90% yield, which on one crystallisation from ethyl acetate afforded orange-red crystals, m.p. 204-205°. (Found: C, 55.43; H, 5.39. $C_{18}H_{20}O_6N_4$ requires C, 55.67; H, 5.15%).

Thanks of the authors are due to Mrs. Chhabi Dutta, M.Sc., University College of Science and Technology, Calcutta, for microanalyses and to Prof. P. C. Dutta for his kind interest.

Department of Organic Chemistry,
Indian Association for the
Cultivation of Science,
Jadavpur, Calcutta 32.

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STUDIES IN TERPENES. PART II. 2-CARENE: PRODUCTION BY ISOMERISATION OF 3 CARENE WITH AQUEOUS SULPHURIC OR GLACIAL ACETIC ACID AND DECYCLISATION-DEHYDROGENATION REACTIONS

By James Verghese*

A simple procedure for the preparation of 2-carene from 3-carene by refluxing with aq. sulphuric or glacial acetic acid is described. 2-Carene over γ-alumina catalyst at 400° suffers decyclisation-dehydrogenation transformations and gives rise to α-terpinene, terpinolene, limonene, sylvestrene and *p*- and *m*-cymenes. Aromatisation of 2-carene in the vapour phase over γ-alumina-chromia catalyst and in the liquid phase with chloranil yielded more *m*- than *p*-cymene. Parallel experiments with 3-carene resulted in more *p*- than *m*-cymene.

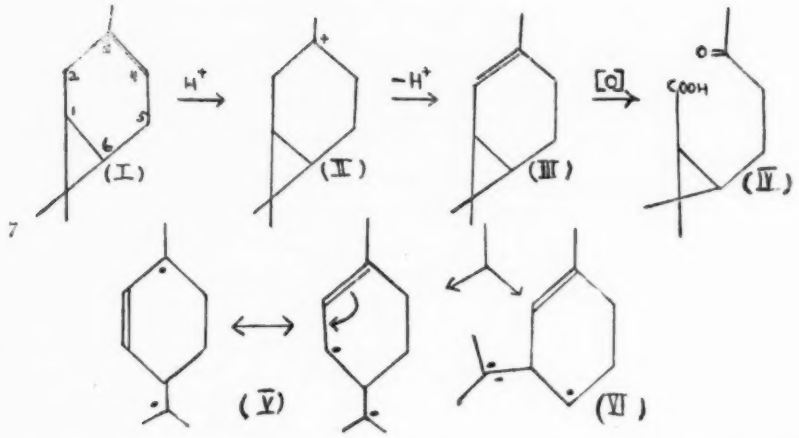
There are a few references in literature concerning the behaviour of 3-carene (I) towards sulphuric and acetic acids. Dilute sulphuric acid did not attack 3-carene on shaking for many days (Semmler and Schiller, *Ber.*, 1927, **60B**, 1591), on heating at 100° for seven days (Simonsen, *J. Chem. Soc.*, 1920, **117**, 574) or even on boiling (Semmler *et al.*, *loc. cit.*). On the other hand, dipentene, γ-terpinene, sylvestrene, *iso*carvestrene (?) and a diterpene were formed when 3 carene was heated to boiling with small amounts of concentrated sulphuric acid (Hellstrom and Ottar, *Kgl. Norske Videnskab, Selskabs Forh.*, 1948, **21**, 156). Decyclisation of 3-carene with ethanolic sulphuric acid yielded α-terpinene and *p*-menthan-3:8 (9)-diene (Jan Krupowicz, Stud. Soc. Torun, Sec. B, 1954, I, No. 2). On refluxing with acetic acid, 3-carene gave α-terpinene (Semmler *et al.*, *loc. cit.*), but on heating with a mixture of acetic-sulphuric acids at 60°, the terpene suffered dimerisation (Simonsen and Gibbs, *J. Chem. Soc.*, 1929, 310).

As can be noted from the literature survey, sulphuric and acetic acids caused decyclisation of 3-carene to afford *p*- and *m*-menthadienes. For this reason, the interaction of these acids on 3-carene with a view to obtaining the bicyclic isomer, 2-carene (III), was investigated.

Contrary to the earlier findings that dilute sulphuric acid does not attack 3-carene, it is shown here, that a five-hour refluxing of the terpene with 5% aqueous sulphuric acid affords an isomerisate containing about 53% of 2-carene. With glacial acetic acid, the extent of rearrangement to 2-carene was considerably less than that with aqueous sulphuric acid; only 20% of 2-carene could be recovered from the mixture.

An adequate explanation which accommodates the rearrangement is found in the expressions (I) to (III).

* Present address: Christian Medical College, Vellore, N. Arcot.



The equation regards the caryl carbonium ion (II), obtained by the addition of proton to the carbon-carbon double bond through its π-electrons, as the intermediate in the formation of 2-carene (Verghese and Yeddanapalli, *J. Sci. Ind. Res.*, 1957, **16A**. 530).

It is evident therefore, that in 3-carene, the methyl-substituted alkene linkage is a more effective nucleophilic reagent than the *gem* dimethyl*cyclo*propane system. Further, the rearrangement of 3- to 2-carene is faster than ring cleavage leading to *p*- and *m*-menthadienes. Thus, in H-acid or L acid catalysed reactions of 3-carene, under mild conditions (cf. Lawrence and Tipper, *J. Chem. Soc.*, 1955, 753 ; Roginiski and Rathmann, *J. Amer. Chem. Soc.*, 1933, **55**, 2800), an allylic rearrangement to 2-carene is to be expected prior to decyclisation (cf. Kretinski *et al.*, *J. Appl. Chem. U.S.S.R.*, 1939, **12**, 878 ; Menon, *J. Madras Univ.*, 1953. B. **23**, No. 1, p. 92).

A *cyclo*propane ring is recognised to be equivalent to a double bond by its physical and chemical properties (Verghese *et al.*, *loc. cit.* ; Menon, *loc. cit.*). Viewed from this angle, the conversion of 3- to 2-carene resembles very much that of γ- to α-terpinene (Gascoigne, *J. Proc. Roy. Soc., N. S. Wales*, 1941, **74**, 359) or of 1 : 4- to 1 : 2-dihydrobenzene (Turnbull U.S.P. 2, 316, 136/1943). Here the *cyclo*propane ring conjugates with the double bond. This rearrangement is of considerable significance relative to the biogenesis of carenes in pines (Aschan, *Annalen*, 1930, **461**, 1).

Finally, the isomerisation technique, described herein, constitutes a simple method for the preparation of 2-carene. Further work in order to get better yields of 2-carene is in progress.

2-Carene gave with Wallach's reagent a transient purple coloration (Aschan, *loc. cit.* ; Simonsen, *J. Chem. Soc.*, 1921, **119**, 1644). Oxidative degradation on the lines recommended earlier (Simonsen, *ibid.*, 1922, **121**, 2292 ; Semmler, *loc. cit.*) afforded D-1 : 1-dimethyl-2-ketobutyl*cyclo*propane 3-carboxylic acid (IV) ; semi carbazone, m.p. 182-83°. The terpene did not respond to Beckmann's chromic acid mixture (Bayer, *Ber.*, 1894, **27**, 815) nor entered into 1 : 4-addition with maleic anhydride

at room temperature in the manner of α-terpinene (unpublished results). Polymerisation with the Friedel-Crafts catalysts gave products of the general formula, $(C_{10}H_{16})_x$, where $x=1$ to 4 (unpublished results). With a variety of organic and inorganic acids, 2-carene underwent two-directional fission of its *cyclo*propane ring, giving rise to *p*- and *m*-menthadienes (unpublished results).

Over γ-alumina catalyst, heated to 400° at a liquid hourly space velocity of 1.0, 2-carene underwent decyclisation-dehydrogenation transformations, resulting in *p*- and *m*-menthadienes and cymenes. Of the menthadienes, α-terpinene, terpinolene, limonene and sylvestrene have been recognised chemically. The biradicals (V) and (VI) arising by the homolytic fission of the C_1-C_7 and C_6-C_7 bonds of 2 carene are probably the precursors of *p*- and *m*-menthadienes respectively ; the cymenes are products of partial dehydrogenation of the dienes.

Aromatisation of 2-carene over γ-alumina-chromia catalyst in the vapour phase afforded more *m*- than *p*-cymene. A two-step process seems to be involved in the aromatisations: decyclisation to *p*- and *m*-menthadienes, followed by dehydrogenation to *p*- and *m*-cymenes respectively. Supporting evidence for this mechanism is provided by the fact that γ-alumina, which is the base for chromia, causes rearrangement of 2-carene to *p*- and *m*-menthadienes ; a similar mechanism seems to be operative in the dehydrogenation with chloranil, as shown by the formation of conjugated dienes. Why 2-carene gives more *m*- than *p*-cymene, and 3-carene more *p*- than *m*-cymene, cannot be explained with the data available.

Experimental

With Mr. S. Gireesan

Reaction of 3-Carene with Aqueous Sulphuric Acid (5%).—3-Carene (b.p./760 mm, 169-71° ; n_D^{30} 1.4693 ; $[\alpha]_D^{30}+9°.52$) (58 g.) and 5% aq. sulphuric acid (0.49 g., *p*H 0.48) were refluxed together at 105-10° for five hours in an oil-bath. The organic layer was separated, washed with water, then with 5% NaOH solution and finally steam-distilled. The volatile portion was dried over anhydrous magnesium sulphate. Combined products from four such runs gave a total yield of 228.8 g. of oil. A two-fold rigorous fractionation of this oil gave a cut with 165-68°/760 mm, n_D^{20} 1.4740, $[\alpha]_D^{30}+4°.74$, yield 53%.

Oxidation of this cut (7.75 g.) in dry acetone (100 c.c.) with $KMnO_4$ (25 g.) furnished the keto-acid (IV), yield 4.65 g. Semicarbazone, yield 10%, m.p. 182-83°.

In the reaction mixture, apart from unchanged 3-carene, maleic anhydride interaction indicated about 12% of conjugated dienes, and 80% ice-cold sulphuric acid treatment (Verghese *et al.*, *J. Sci. Ind. Res.*, 1953, **12B**, 112), about 11% of saturates with cymene smell. The saturates (330 mg.) on oxidation (Verghese *et al.*, *loc. cit.* ; *Curr. Sci.*, 1953, **22**, 112) gave terephthalic acid (39 mg.) and *iso*phthalic acid (36 mg.), showing the presence of *p*- and *m*-cymenes.

Reaction of 3-Carene with Glacial Acetic Acid.—3-Carene (25.70 g.) and glacial acetic acid (7.67 g.) were refluxed together at 126-48° for 40 hours in an oil-bath. The reaction mixture after neutralisation with 5% NaOH solution was steam-distilled ; yield 22.79 g. Fractionation of the steam-distillate gave a cut with b.p. 165-68°, yield 20%. A portion of this cut (3.61 g.) in dry acetone (50 c.c.) on oxidation with $KMnO_4$ (10 g.) afforded the keto-acid (IV) (yield 2.76 g. ; semicarbazone, yield 10%, m.p. 182-83°).

Transformations of 2-Carene over γ-Alumina Catalyst.—Passage of 2-carene (12.60 g.) over γ-alumina catalyst (20 c.c.), heated to 400° and at a liquid hourly space velocity of 1.0, gave a catalysate (yield 9.9 g., n_D^{30} 1.4790, b.p. 170-86°) with 27% α-terpinene (maleic anhydride adduct, m.p. and mixed m.p. 64-65° ; cf. Ipatieff and Pines, *J. Amer. Chem. Soc.*, 1945, **67**, 1227), 18% limonene (terpin hydrate, Bhusan *et al.*, this *Journal, Ind. & News Ed.*, 1944, **7**, 62 ; m.p. and mixed m.p. 118°), 22% saturates containing *p*- and *m*- cymenes, terpinolene (tetrabromide, m.p. 116°), and sylvestrene (dihydrochloride, m.p. 72° ; cf. Alterberg, *Ber.*, 1877, **10**, 1202 ; Wallach, *Annalen*, 1885, **230**, 235).

WITH MR. P. DESIKAN

Dehydrogenation of 2-Carene over γ-Alumina-Chromia Catalyst

2-Carene (8.9 g.) was passed over γ-alumina-chromia catalyst (7% Cr, vol. 20 c.c.), heated to 400° and at a liquid hourly space velocity of 1.0, and the catalysate after agitating with twice its volume of ice-cold 80% H_2SO_4 gave a saturated oil (yield 5.6 g.) which contained 37.40% *p*-cymene and 49.79% *m*-cymene.

Under similar experimental conditions, 3-carene gave 53% *p*-cymene and 43% *m*-cymene (under publication).

WITH MR. S. GIREESAN

Aromatisation of 2- and 3- Carenes with Chloranil

(*i*) *2-Carene.*—A mixture of 2-carene (33.80 g.) and chloranil (10 g.) was refluxed for 5 hours at 160-70° in an oil-bath. The reaction mixture on steam-distillation gave 33.54 g. of an oil which yielded 16% of saturated oil (n_D^{30} 1.4878) containing 5.21% *p*-cymene and 51.72% *m*-cymene.

(*ii*) *3-Carene.*—A corresponding treatment of 3-carene at 165-68° gave 30.96 g. of steam-distillate and 23% saturated oil (n_D^{30} 1.4903) with 31.46% *p*-cymene and 9.20% *m*-cymene.

The conjugated dienes in the steam-distillate of both the experiments amounted to about 15%.

CHEMISTRY DEPARTMENT,
LOYOLA COLLEGE, MADRAS.

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STUDIES IN TERPENES. PART III. CATALYTIC TRANSFORMATIONS OF β-PINENE WITH PHOSPHORIC ACID

By James Verghese*

β-Pinene undergoes two-directional cleavage of the *cyclo*butane ring by interaction with phosphoric acid and gives rise to monocyclics and polymers. The monocyclics contain 25.00% α-terpinene, 10.72% dipentene, 22.80% *p*-cymene, ≮ 2.00% *o*-cymene and ≯ 12.20% menthanes (*p*- and *o*- ?) ; the unaccounted portion definitely included terpinolene and probably γ-terpinene, *o*-menthadienes (?) and *o*- and *p*-menthenes (?). A new procedure is described for analysis of the monocyclics without fractionation. The formation of the various products has been explained by an ionic mechanism.

Although the transformations of β-pinene have been studied with a variety of acid catalysts, the existing literature on the subject does not include the use of phosphoric acid. For that reason, the effect of phosphoric acid upon β-pinene has been investigated.

Experimental

β-Pinene was secured through the courtesy of Hercules Powder Co., Wilmington, Delaware, U. S. A. Before use, the oil was steam-distilled, dried over anhydrous magnesium sulphate, and carefully fractionated. Constants taken for the sample of β-pinene used were : b.p. 165°/760 mm, n_D^{30} 1.4741, d_4^{20} 0.8722, $[\alpha]_D^{30}$ −10°.3. Oxidation of the oil (7 g.) by shaking for ½ hour with a mixture of $KMnO_4$ (24 g.), water (600 g.) and NaOH (5 g.) gave about 1.3 g. of sodium nopinate, and this on neutralisation with H_2SO_4 released nopinic acid which was extracted with ether. A three-fold recrystallisation from benzene furnished nopinic acid melting at 126-27° (Mirov *et al.*, *J. Amer. Pharm. Assoc.*, 1954, **43**, 13). Phosphoric acid (Thomas Tyrer & Co.) used had a specific gravity of 1.75.

Reaction.—β-Pinene (35 g.) and phosphoric acid (3.5 g.) were refluxed together at 168-90° in an oil-bath for 7 hours, precautions having been taken to exclude moisture. There was very little charring and the smell of β-pinene completely disappeared. The reaction mixture was steam-distilled, and the lemon-smelling distillate after drying over anhydrous magnesium sulphate amounted to 17 g. and had n_D^{30} 1.4741, $[\alpha]_D^{30}$ 0° and b.p. 166-89°/760 mm. The product remaining in the distillation flask was taken up in ether, washed with 10% sodium bicarbonate solution, then with water, and after working up in the usual manner was distilled at a reduced pressure to afford 12 g. of a pale yellow, viscous liquid, b. p. 135-50°/3 mm, n_D^{30} 1.5161. This polymeric material was not further examined.

Since the steam-distillate showed no optical rotation, it was evident that β-pinene had completely undergone transformations into inactive compounds ; this was further

*Present address : Chemistry Dept., Christian Medical College, Vellore, N. Arcot.

justified by the boiling range of the steam-distillate which did not include that of β-pinene.

Estimation of α-Terpinene.—This isomer was quantitatively estimated by a method recently developed (under publication). A sample of the oil (8.60 g.) and powdered maleic anhydride (6 g.) were kept in contact in a closed r. b. flask at 75° ± 2° in a water-bath for 2 hours. At the end of this period, the reaction mixture was rendered alkaline with 10% NaOH solution, and the whole steam-distilled (yield 75%). Thus 25% of the oil was fixed up, and corresponded to α-terpinene. From a supplementary experiment, the maleic anhydride adduct of α-terpinene, m.p. and mixed m.p. of 64-65°, as well as the addition product of α-terpinene with maleic acid, m.p. and mixed m.p. of 127-28° were isolated (Ipatieff and Pines, *J. Amer. Chem. Soc.*, 1945, **67**, 1227)

Estimation of Dipentene.—For the estimation of the isomer, the method of Balbiano (*Ber.*, 1915, **48**, 394), modified by Lacrue (*Chem. Zentrl.*, 1942, II, 1795), was employed. A solution of α-terpinene-free oil (6.45 g.) from the above estimation was allowed to stand with an aqueous solution of mercuric acetate (17 g.) and ether (50 c.c.) for 48 hours. The oyster-like mercuric acetate complex formed was separated and the ether-soluble oil worked up in the usual manner. The oil fixed up corresponded to 10.72% of dipentene in the steam-distillate. Further confirmation of the presence of dipentene was obtained by the preparation of terpin hydrate, m.p. and mixed m.p. 115-17°, from a sample of the steam-distillate, freed from α-terpinene according to the directions given by Bhushan *et al.* (this *Journal, Ind. & News Ed.*, 1944, **7**, 62).

Identification of Terpinolene.—This hydrocarbon was identified by the preparation of the tetrabromide, m.p. and mixed m.p. 116°, from a sample of the oil unaffected by mercuric acetate processing.

Composition of the Saturates.—The unsaturates present in a portion of the steam-distillate (4 g.) were destroyed with ice-cold 80% H_2SO_4 and the unaffected oil amounted to 37.0%, b.p. 169-73°/760 mm, n_D^{30} 1.4825. Oxidation of the saturates gave terephthalic acid and *o*-phthalic acid in amounts equivalent to 22.80% *p*-cymene and $\lesssim$ 2.0% *o*-cymene respectively, and nitration (Egloff and Morell, *Ind. Eng. Chem.*, 1926, **18**, 354; cf. Dewar and Read, *J. Chem. Soc.*, 1936, 1781) of the saturates revealed the presence of menthanes (*p*- and *o*- ?) ($\gtrsim$ 12.20%, by difference) in the steam distillate.

Discussion

Transformations of β-pinene by contact with phosphoric acid gave rise to monocyclics and polymers in 49.0% and 35.0% yield respectively on the weight of the starting material. The monocyclics contained 25.0% α-terpinene, 10.72% dipentene, 22.80% *p*-cymene, $\lesssim$ 2.00% *o*-cymene and $\gtrsim$ 12.20% menthanes (*p*- and *o*- ?); the unaccounted portion definitely included terpinolene and probably γ-terpinene, *o*-menthadienes (?) and *o*- and *p*-menthenes (?). This analysis of the monocyclics is exclusively by chemical techniques without fractionation, which is reported to be ineffectual in bringing about a sharp separation of the components even with hundred theoretical plates (Mosher, *J. Amer. Chem. Soc.*, 1947, **69**, 2319).

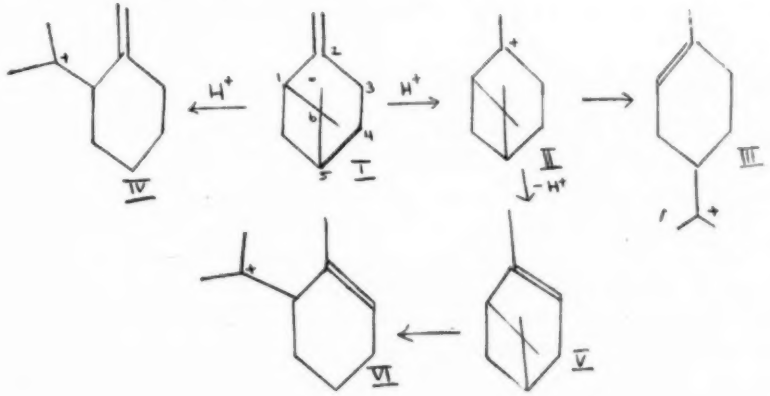
An immediate conclusion that can be drawn from the analytical result is that the *cyclo*butane ring of β-pinene (I) has opened up two-directionally by fission of the C_1-C_6 and C_5-C_6 linkages, resulting in *para* and *ortho* derivatives respectively. Whereas the formation of *para* derivatives is a general feature of acid-catalysed reactions of β-pinene, that of *ortho* derivatives, of which *o*-cymene is chemically identified, is of considerable theoretical interest, it being well known that reactions in the pinane series to afford derivatives of *o*-menthane are rare. This leads to the possibility of obtaining a new set of reaction products from β-pinene, namely derivatives of the *o*-series, and demands a re-investigation of the several decyclisation reactions of β-pinene, reported in literature.

Reaction Mechanism.—Splitting of the *cyclo*butane ring in β-pinene by H^+-catalysed β-fission reaction furnishes the C^+ ion (III) responsible for *p*-menthadienes (Mosher, *loc. cit.*). *p*-Cymene and *p*-menthane can be accounted by hydrogen-transfer reactions (Verghese *et al.*, *J. Sci. Ind. Res.*, 1957, **16B**, 363; Ipatieff *et al.*, *J. Amer. Chem. Soc.*, 1945, **67**, 694; U. S. P. 2,431,756/1947; 2,420,749/1947; Kuryndin, *Z. Priklad. Khim.*, 1948, **21**, 273) expressed by the general equations:

$$2\ C_{10}H_{16}\ (p\text{-menthadienes}) \longrightarrow C_{10}H_{14}\ (p\text{-cymene}) + C_{10}H_{18}\ (p\text{-menthenes})$$
$$3\ C_{10}H_{16}\ (p\text{-menthadienes}) \longrightarrow 2C_{10}H_{14}\ (p\text{-cymene}) + C_{10}H_{20}\ (p\text{-menthane})$$
$$3\ C_{10}H_{18}\ (p\text{-menthenes}) \longrightarrow 2\ C_{10}H_{20}\ (p\text{-menthane}) + C_{10}H_{14}\ (p\text{-cymene})$$

A similar mechanism would explain the production of *o*-cymene and *o*-menthane.

On the other hand, direct cleavge of the 4-membered ring in β-pinene with acceptance of proton resulting in C^+-ion (IV) seems to be the primary step in the formation of *o*-derivatives. This mode of decyclisation is justified because *cyclo*butane ring is a nucleophilic reagent.



It is likely that these transformations of β-pinene might have been preceded by a rearrangement to α-pinene (V), in which case, the same explanation holds good, the precursor of the *o*-series being, however, the organic ion (VI).

Of the two types of ring fission, the β-bond splitting is the more favoured route, for such a reaction involves participation of the π-electrons of the double bond in β-pinene which are more polarisable than the electron pairs of the C—C bond of the *cyclo*butane ring. This would explain why in many of the decyclisation reactions of β-pinene, the formation of *o*-derivatives has been overlooked.

A comprehensive scheme of work is in progress with a view to isolating *ortho* derivatives in acid-catalysed transformations of β- and α-pinenes.

CHEMISTRY DEPARTMENT,
LOYOLA COLLEGE, MADRAS.

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DETECTION OF CHELATION BY MEANS OF SPECTRAL AND DIPOLE MOMENT MEASUREMENTS

By K. Aparajithan and V. Baliah

The ultraviolet absorption spectroscopic and dipole moment studies indicate the existence of a weak intramolecular hydrogen bond in *o*-hydroxydiphenylsulphone. There is no significant change in the dipole moment of a strongly chelated compound, while there is a significant increase in the moment of a weakly chelated compound with change of solvent from benzene to dioxan.

In the present work, two factors have been studied to detect chelation. One is the effect of concentration on chelation and the other, the effect of chelation on dipole moment. The effect of concentration on chelation has been investigated spectroscopically. To study the effect of chelation on dipole moment, the dipole moments of *o*-, *m*- and *p*-nitrophenol as well as those of *o* , *m* and *p*-hydroxydiphenylsulphone have been determined. The effect of solvent on dipole moments was also studied to gain knowledge on the formation and strength of hydrogen bonds.

Experimental

Hydroxydiphenylsulphones (*o*- and *m*-) were prepared by the method of Heppenstall and Smiles (*J. Chem. Soc.*, 1938, 899) ; the *p*-isomer was prepared as described by Aleykutty and Baliah (this *Journal*, 1954, **31**, 513).

B.D.H. "Analar" benzene was dried over sodium wire for a day. It was decanted into a clean dry flask and distilled over P_2O_5, using an all-glass distillation assembly provided with a calcium chloride guard-tube. E. Merck's pure dioxan was mechanically shaken with excess of KOH pellets for 3 hours and the aqueous layer removed. It was then allowed to stand over solid KOH for 24 hours in order to remove most of the residual water. It was refluxed over excess of sodium for 9-12 hours until reaction had ceased and sodium remained bright. It was then distilled over sodium. The fraction distilling at 100.75° – 101.25° was collected. The last 100 c. c. was not distilled, as dioxan is known to explode on complete evaporation, especially when dry.

Dipole Moment Determination.—The dielectric constant of each solution was measured employing a dielectrometer (Dekameter DKO3) designed by Dr. Habil Slevogt and manufactured by Wissenschaftlich Technische Werkstatten. Operated on 220 volts A.C. mains (50 to 60 cycles) and working on the resonance principle, it had a fixed frequency of 1.8 megacycles. The dielectric cell of suitable capacitance, supplied by the manufacturers, was used. The temperature of the solution was controlled by circulation of water with Hoppler's ultrathermosta .

The densities of the solutions were measured in the customary manner.

Ultraviolet Absorption Measurements.—The ultraviolet absorption spectra were determined with a Beckman quartz spectrophotometer, Model DU. Ethanol refers to 95% ethanol.

Calculation of the Dipole Moment.—From the measured dielectric constant (ϵ_{12}) and density (d_{12}) of each solution, constants α and β were calculated from the equations:

$$\epsilon_{12} = \epsilon_1 (1 + \alpha w_2);$$
$$d_{12} = d_1 (1 + \beta w_2),$$

where ϵ_1 and d_1 are the dielectric constant and density of the solvent, and w_2 is the weight fraction of the solute. The molar polarisation of the solute at infinite dilution ($_\infty P_2$) was calculated from the relation (Cumper and Walker, *Trans. Faraday Soc.*, 1956, **52**, 193):

$$_\infty P_2 = M_2 \frac{(\epsilon_1 - 1)}{(\epsilon_2 + 2)} \frac{(1 - \beta)}{d_1} + \frac{3M_2 \alpha \epsilon_1}{d_1 (\epsilon_1 + 2)^2}.$$

The dipole moment was obtained from the usual expression:

$$\mu = 0.01281 [(_\infty P_2 - R_D) T]^{\frac{1}{2}} \text{ debyes},$$

where R_D is the molar refraction of the solute and T is the temperature of measurement in degrees Absolute.

All measurements were made at 30° ± 0.05°. The experimental results are recorded in Table I. Unless otherwise indicated, the determinations were made in dioxan.

TABLE I

w_2.	$\epsilon_{12}-\epsilon_1$.	$d_{12}-d_1$.	w_2.	$\epsilon_{12}-\epsilon_1$.	$d_{12}-d_1$.	w_2.	$\epsilon_{12}-\epsilon_1$.	$d_{12}-d_1$.
o-Nitrophenol:			*m*-Nitrophenol:			*p*-Nitrophenol:		
$\alpha=4.172$. $\beta=0.2296$. $_\infty P_2=242.5$cc.			$\alpha=7.965$. $\beta=0.02249$. $_\infty P_2=435.6$cc.			$\alpha=11.76$. $\beta=0.2514$. $_\infty P_2=627.2$cc.		
$R_D=33.16$ c.c. $\mu=3.23D$.			$R_D=33.16$ c.c. $\mu=4.47D$.			$R_D=33.16$ cc. $\mu=5.43D$.		
0.014690	0.137	0.003520	0.016900	0.305	0.004110	0.015470	0.415	0.003840
0.012290	0.115	0.002995	0.015410	0.275	0.003940	0.014080	0.380	0.003768
0.010330	0.097	0.002400	0.013000	0.236	0.002730	0.011700	0.314	0.003200
0.007025	0.069	0.001860	0.011020	0.199	0.002610	0.006956	0.190	0.001665
0.004777	0.045	0.000930	0.005797	0.107	0.001190			
o-Hydroxydiphenylsulphone:						*o*-Hydroxydiphenylsulphone (in benzene):		
$\alpha=6.525$. $\beta=0.2203$. $_\infty P_2=611.3$ c.c.						$\alpha=4.411$. $\beta=0.2928$. $_\infty P_2=502.6$ c.c.		
$R_D=60.21$ c.c $\mu=5.24D$.						$R_D=60.21$ c.c. $\mu=4.69D$.		
0.014093	0.208	0.003290				0.015400	0.163	0.004400
0.012680	0.189	0.002965				0.014290	0.146	0.003677
0.008441	0.125	0.001898				0.012080	0.121	0.003170
0.008023	0.122	0.001795				0.010550	0.111	0.002842
0.006772	0.103	0.001420				0.007071	0.075	0.001645
						0.006564	0.067	0.001440
m-Hydroxydiphenyl sulphone:			*p*-Hydroxydiphenylsulphone:			*o*-Methoxydiphenylsulphone (in benzene):		
$\alpha=7.018$. $\beta=0.2144$. $_\infty P_2=653.7$ c.c.			$\alpha=8.812$. $\beta=0.1387$. $_\infty P_2=812$ c.c.			$\alpha=6.867$. $\beta=0.3504$. $_\infty P_2=781.4$ c.c.		
$R_D=60.21$ c.c. $\mu=5.43D$.			$R_D=60.21$ c.c. $\mu=6.11D$.			$R_D=54.58$ c.c. $\mu=6.01D$.		
0.019360	0.311	0.004379	0.025520	0.499	0.005830	0.016900	0.264	0.004895
0.016870	0.266	0.003665	0.020190	0.400	0.003925	0.014380	0.228	0.004290
0.014220	0.226	0.003215	0.009200	0.187	0.000685	0.012300	0.196	0.003700
0.007188	0.116	0.001496	0.006219	0.126	0.000440	0.010880	0.171	0.003610
						0.009249	0.145	0.002910

Discussion

Forbes and Templeton (*Chem. & Ind.*, 1957, 77) found that associated compounds (*i. e.* compounds with intermolecular hydrogen bonding) did not obey Beer's law and that the intermolecular hydrogen bonding caused an increase in the molar absorption intensity without appreciably affecting the wave-lengths of maximal absorption. They also found that in the case of chelated compounds, like salicylic acid. the molar absorption intensity was independent of concentration. The data obtained for *o*- and *p*-hydroxydiphenylsulphones, and *o*- and *p*-nitrophenols in the present study are recorded in Table II.

Table II

(Conc. $c = 1.8 \times 10^{-5}$ to 3.6×10^{-5} moles/litre)

Compound.	Solvent.	Conc.	*$\lambda_{max.}$	$\epsilon_{max.}$
o-Hydroxydiphenylsulphone	*cyclo*Hexane	7 *c*	238 mμ	10,700
		4 *c*	237	10,600
		2 *c*	238	10,600
p-Hydroxydiphenylsulphone	Dioxan	5 *c*	253	17,100
		4 *c*	253	16,700
		2 *c*	253	16,700
o-Nitrophenol	Dioxan	8 *c*	273	6,900
		4 *c*	274	6,800
		2 *c*	274	6,900
p-Nitrophenol	Dioxan	6 *c*	304	11,600
		4 *c*	304	11,300
		2 *c*	304	11,100

* The high intensity band only is shown.

The data clearly indicate the non-existence of any significant association in the case of *o*-hydroxydiphenylsulphone and *o*-nitrophenol, and thereby provide indirect evidence for the existence of intramolecular hydrogen bonding. But the data for *p*-hydroxydiphenylsulphone and *p*-nitrophenol do not convincingly prove the existence of intermolecular hydrogen bonding in them though such bonding is known to exist in these compounds from other evidence. This apparent anomaly might be due to the reason that the solvent employed was dioxan (an inactive solvent like *cyclo*hexane could not be used for *p*-hydroxydiphenylsulphone and *p*-nitrophenol, as their solubility in it is very low). Dioxan, being an oxygenated solvent, seems to form intermolecular hydrogen bonding with solute molecules, thereby destroying the weak intermolecular hydrogen bonding among the solute molecules.

The above view about the behaviour of dioxan gains support from the spectral behaviour of chelated and non-chelated phenols in various solvents, as shown in Table III.

TABLE III

Solvent effect on the ultraviolet absorption spectra.

Compound.	Solvent.	$\lambda_{max.}$	$\epsilon_{max.}$
o-Nitrophenol	Hexane[1]	346 mμ	3,900
		271	7,600
	Ethanol[1]	343·5	3,600
		273	6,600
	Dioxan[4]	348	3,600
		274	6,900
p-Nitrophenol	*cyclo*Hexane[4]	287	10,400
	Ethanol[2]	314	13,000
	Dioxan[4]	304	11.200
o-Hydroxydiphenyl-sulphone	*cyclo*Hexane[4]	295	4,500
		238	10,700
	Ethanol[3]	295	4,200
		233	12,600
	Dioxan[4]	293	4,200
		236	11,000
p-Hydroxydiphenyl-sulphone	*cyclo*Hexane[3]	247	13,000
	Ethanol[3]	255	14,100
	Dioxan[4]	253	16,700

1. Burawoy *et al.*, *J. Chem. Soc.*, 1955, 3727.
2. *Iedm*, *ibid.*, 1955, 3722.
3. Baliah and Mathew, this *Journal*, 1957, **34**, 364.
4. Data obtained in the present investigation.

The B- and K-bands of phenols in which no chelation occurs shift to longer wave-lengths with increase in the dielectric constant of the solvent (Burawoy *et al.*, *J. Chem. Soc.*, 1955, 3723). This is seen to be the case for *p*-nitrophenol and *p*-hydroxydiphenylsulphone. On the other hand, the B-band of the *o* hydroxydiphenylsulphone is almost unaffected with change of solvent. The K-band is, however, shifted slightly to shorter wave-lengths with increase in the dielectric constant of the solvent. This is significant in view of the fact that the K-band of *o*-nitrophenol undergoes a very slight red shift with increase in the dielectric constant of the solvent. The explanation for this seems to be that the $-SO_2-$ group forms a weak intramolecular hydrogen bond and this bond may be broken to a considerable extent in oxygenated solvents like ethanol and dioxan.

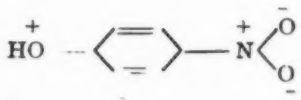
The dipole moments of *o*-, *m*- and *p*-nitrophenol in benzene and dioxan are shown in Table IV.

TABLE IV

Nitrophenol.	Moments (in *D*) in Benzene*.	Dioxan.
o-	3.10	3·23
m-	3 90	4·47
p-	5.05	5·43

* Data from Table of Dipole Moments, *Trans. Faraday Soc.*, 1934, Appendix.

The dipole moment of nitrobenzene in benzene is 3.98*D* (C. P. Smyth, "Dielectric Behaviour and Structure", McGraw Hill, New York, 1955, p. 314). The introduction of OH group into the *ortho*, *meta* and *para* positions has altered this value to 3.10*D*, 3.90 *D* and 5.05 *D*, respectively. The much higher value for *p*-nitrophenol is certainly due to the contribution of the structure :



to the ground state of the molecule. Since a similar resonance interaction is possible in the case of *o*-nitrophenol also, one might expect a high dipole moment for *o*-nitrophenol too. But the observed value 3.10 *D*, which is less than the moment of even nitrobenzene, must be due to intramolecular hydrogen bonding. It is also significant to note that a change of the solvent from benzene to dioxan does not alter the moment very much (increase is only 0.13*D*). For *m*- and *p*-nitrophenols, the values in dioxan are 0.57 *D* and 0.38 *D* higher, respectively, than in benzene. This is exactly what is to be expected if we bear in mind the conclusions arrived at from the spectroscopic data, namely, that *o*-nitrophenol retains chelation even in dioxan leading to no significant interaction with the solvent while *p*-nitrophenol (and possibly *m*-nitrophenol) forms intermolecular hydrogen bonding with dioxan. Such hydrogen bonding should raise the moments of *m*- and *p*-nitrophenols. This view can be substantiated by the investigations of Few and Smith (*J. Chem. Soc.*, 1949, 753, 2663) as well as Curran and Estok (*J. Amer. Chem. Soc.*, 1950, **72**, 4575).

TABLE V

Hydroxydiphenylsulphone.	Moments (in *D*) in	
	Benzene.	Dioxan.
m-	4.69	5.25
o-	...	5.43
p-	...	6.11

The dipole moments of *o*-, *m*- and *p*-hydroxydiphenylsulphones are recorded in Table V. The moments of *m*- and *p*-hydroxydiphenylsulphones could not be determined in benzene as their solubility was very low. However, the value of 4.69 *D* obtained for the *ortho* isomer is less than 5.05 *D*, which is the moment of diphenylsulphone (DeVries and Rodebush, *J. Amer. Chem. Soc.*, 1931, **53**, 2888). This clearly proves the existence of intramolecular hydrogen bonding in *o*-hydroxydiphenylsulphone. That the introduction of a chelation-causing *ortho*-hydroxyl group lowers the moment of a compound can be seen as a general phenomenon from the values collected from literature for the pairs of compounds listed in Table VI.

TABLE VI

Moments in benzene solution.

Salicylaldehyde[1]	2.86 *D*	Benzaldehyde[4]	2.98 *D*
o-Hydroxyacetophenone[2]	2.78	Acetophenone[5]	2.89
o-Fluorophenol[3]	1.16	Fluorobenzene[6]	1.45
o-Chlorophenol[3]	1.33	Chlorobenzene[6]	1.64
o-Bromophenol[6]	1.36	Bromobenzene[6]	1.56

1. Lumbroso, *Chem. Abst.*, 1954, **48**, 5783.
2. Lutskii, *ibid.*, 1949. **43**, 6020.
3. Anzilotti and Curran, *J. Amer. Chem. Soc.*, 1943, **65**, 607.
4. Calderbank and Le Fevre, *J. Chem. Soc*, 1949, 1462.
5. Le Fevre and Le Fevre, *ibid.*, 1950, 1829.
6. Table of Dipole Moments, *loc. cit.*

It may be of interest to note that while chelation-causing *ortho*-hydroxyl group lowers the moment of a compound, a group like methoxyl, which cannot cause chelation, actually increases the dipole moment of a compound when present in the *ortho* position. This can be seen from the values recorded in Table VII.

TABLE VII

Moments in benzene solution.

o-Fluoroanisole[1]	2.31 *D*	Fluorobenzene[5]	1.45 *D*
o-Chloroanisole[1]	2.50	Chlorobenzene[5]	1.64
o-Bromoanisole[1]	2.47	Bromobenzene[5]	1.56
o-Methoxybenzaldehyde[2]	4.19	Benzaldehyde[5]	2.98
o-Methoxyacetophenone[3]	3.99	Acetophenone[5]	2.89
o-Nitroanisole[4]	4.80	Nitrobenzene[4]	3.98
o-Methoxydiphenylsulphone	6.01	Diphenylsulphone	5.05

1,2,3,4—See references 3, 1, 2, 6 of Table VI, respectively. 5—See Table VI.

The effect of solvent on the dipole moment of *o*-hydroxydiphenylsulphone (see Table V) is interesting to study. There is a significant increase in moment (0.56 *D*) by changing the solvent from benzene to dioxan. This is in contrast to what has been observed for *o*-nitrophenol. The explanation for this seems to be that in the case of *o*-nitrophenol, chelation is strong and is not much affected in an oxygenated solvent like dioxan. In the case of *o* hydroxydiphenylsulphone chelation is weak and is considerably broken in dioxan leading to hydrogen bonding between the solute and solvent. Thus, the behaviour of a weakly chelated compound in dioxan will be more like a non chelated phenol. The findings of Curran (*J. Amer. Chem. Soc.*, 1945, **67**, 1835; see also Anzilotti and Curran, *loc. cit.*) amply support such a view.

DEPARTMENT OF CHEMISTRY,
ANNAMALAI UNIVERSITY,
ANNAMALAINAGAR.

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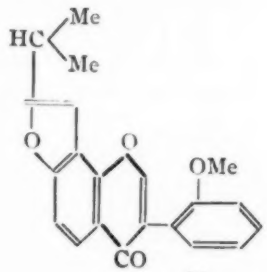
CHEMICAL INVESTIGATION OF *MUNDULEA SUBEROSA* BENTH. PART II. CONSTITUTION OF MUNETONE, THE PRINCIPAL CRYSTALLINE PRODUCT OF THE ROOT BARK

By Narendra Lal Dutta*

On the basis of the isolation of formic acid, *o*-methoxybenzoic acid, *iso*butyric acid, *iso*tubaic acid and a phenolic ketone, named as "munetol", from various degradation products of munetone, the structure of the latter has been assigned as 2-methoxy-7 : 8-(2-*iso*propyl-4 : 5-furano)-*iso*flavone.

In Part I of this series (this *Journal*, 1956, **33**, 716) the isolation of three crystalline constituents and general descriptions of the physical and chemical properties of munetone, $C_{21}H_{18}O_4$, m.p. 192-93°, the principal crystalline product of the root bark of *Mundulea suberosa*, were reported. The *iso*flavone nature of munetone was also shown by its conversion, on alkaline hydrolysis, to formic acid and munetol, $C_{20}H_{20}O_4$, m.p. 128°, a derivative of *o*-hydroxyphenylbenzyl ketone. The present paper embodies the results of subsequent investigations on the constitution of munetone, which are principally based on a close study of its action on alkaline hydrogen peroxide under various conditions. As a result, the following constitution has been tentatively arrived at for munetone.



(I)

On mild acetylation with acetic anhydride and pyridine at ordinary temperature, munetol yielded an acetyl derivative, m.p. 103°. This acetyl compound or munetol itself, when treated with acetic anhydride and sodium acetate under drastic condition, produced the 2-methyl*iso*flavone derivative, $C_{22}H_{20}O_4$ (*loc. cit.*), which on mild alkaline hydrolysis regenerated munetol, and from the aqueous fraction, acetic acid was detected (Feigl, "Spot Tests", 1954, Vol. II, pp.245, 247). From the reactions so far studied, the *iso*flavone nature of munetone has been reasonably established ;

* Present address : Department of Chemistry, Duke University, Durham, N.C., U.S.A.

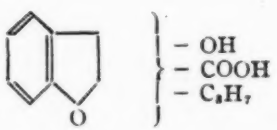
finally, this has been confirmed by its synthesis from munetol with ethyl orthoformate in presence of pyridine and piperidine (Iyer *et al.*, *Proc. Ind. Acad. Sci.*, 1951, **33A**, 116).

From drastic alkaline hydrolysis of munetol, no recognisable product could be identified. On fusion with caustic potash, munetone produced a liquid acid, which was subsequently identified as *iso*butyric acid by the formation of an anilide, $C_{10}H_{13}ON$, m.p. 105° (mixed m.p.).

So far three oxygenic functions in munetone have been accounted for—two in the pyrone ring and another in a methoxy group. All attempts to bring the fourth oxygen into reaction have failed. It thus appeared to be present as a stable ether linkage in the molecule. Infra-red absorption spectra of munetone and munetol (*vide infra*) suggest the presence of a five- or six-membered oxygen ring in the molecule.

Oxidative experiments finally revealed the nature of the whole molecule in munetone. Oxidation of munetol with hydrogen peroxide in alkaline solution produced an acid, identical with *o*-methoxybenzoic acid (mixed m.p. 99-100°), along with a phenolic product, crystallising from alcohol in lemon-yellow needles, m.p. 139°. This phenol, on drastic acetylation, yielded a product crystallising as colorless needles from methyl alcohol, m.p. 190°, analysing as $C_{19}H_{16}O_4.H_2O$. This was not further studied, due to lack of sufficient material.

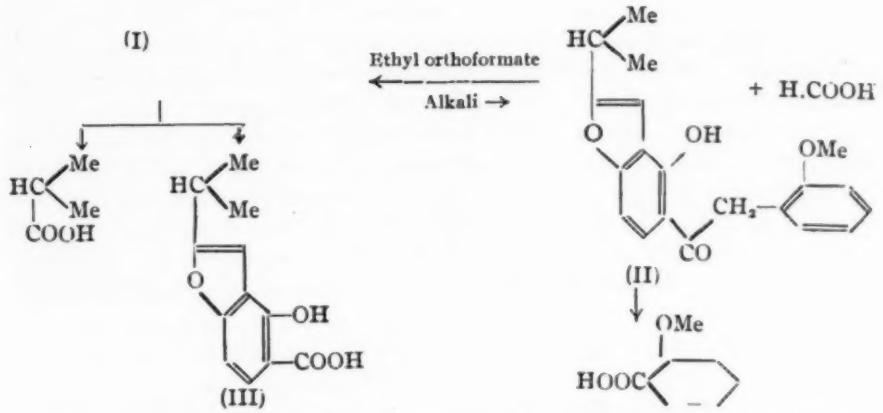
Oxidation of munetone, with alkaline hydrogen peroxide under controlled condition, produced an acid as colorless thick prisms from dilute acetic acid, $C_{12}H_{12}O_4$, m.p. 183-84°. An alcoholic solution of this acid produced a deep blue coloration with ferric chloride. This intense ferric reaction showed the presence of a hydroxyl group in the compound in proximity to a carboxyl group. It easily formed an acetyl derivative, m.p. 153-54°; with diazomethane it formed a methoxy ester which on hydrolysis produced the methyl ether of the acid, m.p. 114°. The infra-red spectra of the acid indicate the possibility of a furan ring in the molecule. Assuming that it is a benzofuran derivative, the formula of the acid reduces to



The isolation of *iso*butyric acid from the alkali fusion product of munetone shows that the *iso*propyl group must have been attached to the above acid.

A search in the literature revealed that the above acid appeared to be identical with *iso*tubaic acid (rotenic acid), isolated by Takei (*Ber.*, 1928, **61**, 1003) and Haller and LaForge (*J. Amer. Chem. Soc.*, 1930, **52**, 2480) and finally synthesised by Reichstein (*Helv. Chim. Acta*, 1933, **16**, 121). The identity was confirmed by a direct comparison of the acid with a synthetic sample of *iso*tubaic acid.

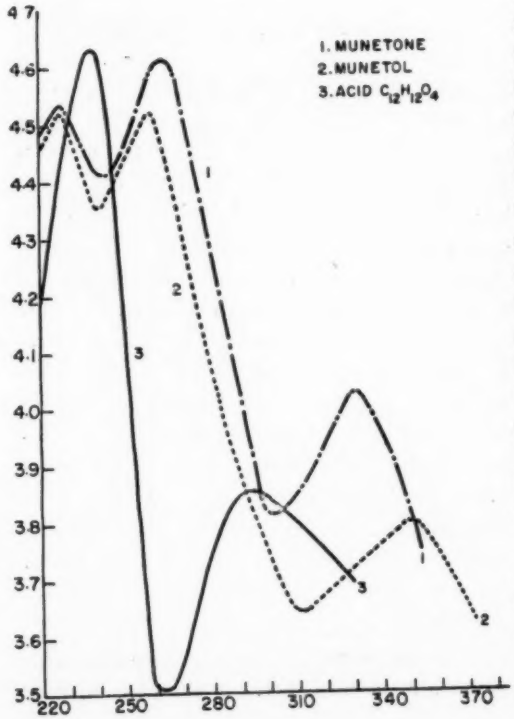
The degradation products can be diagramatically shown as follows:



In course of the oxidation of munetone for the isolation of *iso*tubaic acid, a neutral compound was obtained, crystallising from a mixture of ethyl acetate and acetone in colorless prisms, m.p. 260°, which analysed for $C_{21}H_{20}O_4$. It was not further studied due to lack of sufficient material.

The ultraviolet spectra of the compounds (munetone, munetol and the acid $C_{12}H_{12}O_4$) were taken in alcoholic solution, using a Beckman spectrophotometer Model DU (vide Fig. 1). Infrared spectra of munetone (I), munetol (II) and the acid $C_{12}H_{12}O_4$ (III) were taken with a Grubb Parson's single beam instrument using rock salt prism. Both (I) and (II) showed strong absorption in the 6.1–6.2μ region, which is characteristic of a conjugated carboxyl group. A band with an absorption maximum at 3.09μ showed strong hydrogen bonding (hydroxyl group) which is present in (II) and (III) and not in (I). Bands with absorption maxima at 8.68μ, 9.28μ and 9.51μ in (I), 8.5μ and 9.33μ in (II) and 8.74μ and 9.30μ in (III) may be due to the presence of a furan ring in the compounds.

FIG. 1



The structure of munetone, thus established, provides a possible explanation of the biogenetic route of the formation of rotenone type of compounds in nature. Rotenone possesses an *iso*flavanone nucleus. Therefore it may be assumed that an *iso*flavone or an *iso*flavanone structure

is the intermediate in the biosynthesis of chromano-chromanone type of compounds in nature. Munetone has been shown to contain a furan ring, fused to the benzopyrone nucleus at the same positions as that of rotenone, sumatrol, malaccol, elliptone, etc. The isolation of munetone, a 2′-methoxy*iso*flavone in the present case, from a rotenone bearing plant, indicates that the $-CH_2O$ bridge between 2- and 2′-carbon atoms in rotenone might be formed by this route, namely from 2′-methoxy group. This also indicates that munetone is an intermediate in the biosynthesis of rotenone type of compounds. The active hydrogen atom attached to the 2-carbon atom is likely to play an important part in the formation of the $-CH_2O-$ bridge with the 2′-methoxy group, through a molecular rearrangement.

Experimental

Acetylation of Munetol under mild condition.—In a solution of munetol (100 mg.) in acetic anhydride (4 c.c.), pyridine (4 drops) was added and the reaction mixture was kept for 24 hours at room temperature. On addition of ice and water, a solid precipitate slowly appeared, which was filtered, washed with water, dried and crystallised from dilute methyl alcohol, when the acetyl derivative was obtained as colourless rectangular prisms, m.p. 103°, yield 100 mg. It did not exhibit any coloration with ferric chloride-alcohol. (Found: C, 72.42; H, 6.0. $C_{22}H_{22}O_5$ requires C, 72.11; H, 6.05%).

Fusion of Munetone with KOH: *Isolation of* iso*Butyric Acid.*—Munetone (1 g.) was added in small quantities with stirring to fused KOH (16 g.) at 260°. When the addition was complete, heating was continued for 15 minutes more. The melt on cooling was dissolved in ice-water and saturated with carbon dioxide, when there was a dark coloured precipitate. It was extracted with ether and the ethereal solution washed with water and dried over anhydrous sodium sulphate. On removing ether, the residue left was a dark-coloured viscous material which could not be crystallised.

The aqueous solution containing the acidic fraction was acidified with H_2SO_4 (dil.) and extracted with ether. The ethereal solution was dried and on removal of the solvent, a dark brown semi-solid mass was obtained having an unpleasant odour. This was steam-distilled and the distillate had the characteristic smell of a lower fatty acid. It was extracted with ether, dried and was freed of the solvent, when an almost colorless liquid (0.08 g.) was obtained, which was converted into an anilide in the usual way. The anilide was obtained as colorless long needles, m.p. 104-105°. There was no depression in mixed melting point of the substance with an authentic sample of *iso*butyric anilide. (Found: N, 8.5. Calc. for $C_{10}H_{13}ON$: N, 8.58%).

Oxidation of Munetol with H_2O_2.—Munetol (1.2 g.), dissolved in methyl alcohol (100 c.c.), was treated under mechanical stirring with 8 c.c. of 50% aqueous KOH, followed by the dropwise addition of 10 c.c. of 30% aqueous hydrogen peroxide (100 vols.).

The oxidation was ontinued for 48 hours at room temperature, whereupon the solution tested onlyfaintly oxidising to potassium iodide paper. A saturated aqueous

sodium bisulphate solution (2 c.c.) was slowly added with cooling ; the mixture was then neutral to potassium iodide paper and basic to litmus. On removing the solvent under reduced pressure, the aqueous solution was acidified with H_2SO_4 (dil.) and extracted with ether. The ethereal extract (A) was washed with a saturated aqueous sodium bicarbonate solution. The bicarbonate washings were acidified and extracted with ether, dried and freed of the solvent, when a dark semi-solid mass was obtained. This was crystallised twice from water (charcoal) when colorless prisms of *o*-methoxybenzoic acid was obtained (mixed m.p. 99-100°). (Found : C, 63.38 ; H, 5.58 ; OMe, 20.0. Calc. for $C_8H_8O_3$: C, 63.2 ; H, 5.3 OMe, 20.4%).

The ethereal extract (A), after removal of the acid fraction, was separated into neutral and phenolic fractions by extraction with 2% KOH solution in water. Only traces of an amorphous material was found in the neutral fraction. The phenolic fraction was acidified and extracted with ether, which was dried and freed of the solvent, when a yellow solid was obtained, crystallising from dilute alcohol (charcoal) in lemon-yellow needles, m.p. 139°. It was soluble in 2% aqueous alkali and gave a deep green colour with ferric chloride-alcohol. (Found : C, 71.45, 71.42 ; H, 5.53, 5.2. $C_{17}H_{16}O_4$ requires C, 71.82 ; H, 5.67%).

The above phenol (m.p. 139°) on treatment with acetic anhydride and fused sodium acetate under drastic condition in the usual way, yielded a product, crystallising from methyl alcohol in clusters of colorless needles, m.p. 190°. (Found : C, 70.10 ; H, 5.96. $C_{19}H_{16}O_4.H_2O$ requires C, 69.99 ; H, 5.52%).

Oxidation of Munelone with H_2O_2.—In a solution of munetone (1 g.) in methyl alcohol (200 c.c.) under reflux, aqueous KOH (1 g. in 5 c.c. water) was added in small quantity at a time (1 c.c. in every half hour), followed by the addition of small quantities of hydrogen peroxide (30%, 100 vols., 1 c.c. at a time, total 9 c.c.) in the course of 4 hours. The solution was occasionally tested which was kept just alkaline. The reaction mixture was left overnight at room temperature. The yellow solution, thus obtained, was freed of methyl alcohol under vacuum and water (20 c.c.) was added. There was a small amount of an insoluble precipitate which was removed in ether. The ethereal solution was dried and freed of the solvent. From the residue a small amount of a product was obtained, crystallising from a mixture of ethyl acetate and acetone as colorless prisms, m.p. 245°. The alkaline aqueous layer was carefully acidified with H_2SO_4 (dil.) when a thick liquid was obtained which was extracted with ether. The ethereal solution was treated with sodium bicarbonate solution and the aqueous fraction was acidified, which was extracted with ether, dried and freed of the solvent, when a thick oily substance was obtained. On maceration with water, it came out as a solid which was filtered and dried (yield 0.3 g.). On repeated crystallisations from dilute acetic acid, it was obtained as colorless thick prisms, m.p. 183-84°. It gave an intense blue coloration with ferric chloride-alcohol. (Found : C, 65.72 ; H, 5.49 ; equiv., 223 $C_{12}H_{12}O_4$ requires C, 65.44 ; H, 5.49% ; equiv., 220). OMe group was found to be absent.

A mixed melting point determination of the above acid with synthetic *iso*tubaic acid was found to give no depression.

Acetylation of the Acid, $C_{12}H_{12}O_4$.—The acetyl derivative of the acid was prepared in the usual way with acetic anhydride and pyridine at room temperature for 24 hours. It was crystallised from dilute methyl alcohol as colorless needles, m.p. 154-55° and did not give any coloration with ferric chloride-alcohol. (Found : C, 64.33 ; H, 5.7. $C_{14}H_{14}O_5$ requires C, 64.11 ; H, 5.38%).

Methyl Ether of the Acid, $C_{12}H_{12}O_4$.—The acid (100 mg.) was taken in dry ether and an ethereal solution of excess of diazomethane added and left at room temperature for 48 hours. The oily residue which was left after removal of the solvent, was hydrolysed with alcoholic potassium hydroxide, and on acidification yielded the methyl ether, crystallising from dilute methyl alcohol in colorless prisms, m.p. 114-15°. It did not give any coloration with ferric chloride-alcohol. (Found : C, 66.62 ; H, 5.95. $C_{13}H_{14}O_4$ requires C, 66.65 ; H, 6.02%).

Attempted Demethylation of Munetone.—Several attempts were made to demethylate munetone under various conditions, but in each case a resinous product was obtained from which no crystalline compound could be isolated.

Synthesis of Munetone from Munetol.—To a solution of munetol (100 mg.) in dry pyridine (2 c.c.) were added ethyl orthoformate (0.2 c.c.) and piperidine (2 drops) and the mixture was refluxed in an oil-bath at 120° for 8 hours. After keeping overnight, water was added to the reaction mixture and the resulting emulsion on treatment with a few drops of dilute HCl gave a light brown precipitate which was collected and washed with water and crystallised from 50% alcohol (charcoal), when it was obtained in colorless prisms, m.p. 192° (yield 60 mg.). There was no depression in mixed melting point of the compound with munetone. (Found : C, 74.99 ; H, 5.50. Calc. for $C_{21}H_{18}O_4$: C, 75.43 ; H, 5.43%).

The author wishes to express his thanks to Prof. R. C. Shah for his kind interest in the work. He is thankful to Prof. Reichstein for a specimen of *iso*tubaic acid. He is also thankful to Dr. G. D. Shah, Mr. V. S Pansare and Mr V. N. Mulay for the microanalyses recorded in this paper and to Dr. Mrs. S. Dasgupta for the infra-red absorption spectra.

NATIONAL CHEMICAL LABORATORY,
POONA-8.

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COAGULATION AND ELECTROKINETIC POTENTIAL OF URANYL FERROCYANIDE SOL

By B. N. Ghosh and P. K. De

The apparent electrokinetic potential, ζ_a, of an uranyl ferrocyanide sol has been measured both by the electro-osmotic and electrophoretic methods in the region of slow coagulation using Smoluchowski's equation in the presence of equicoagulating concentrations of electrolytes containing counter ions of different valency. ζ_a has also been measured in the region of rapid coagulation by the electro-osmotic method. The true electrokinetic potential, ζ, has been evaluated by applying surface conductance correction with the help of the equation,

$$\frac{1}{\zeta_a} = \frac{1}{\zeta} + m.\frac{1}{S}$$

where m is a constant involving surface conductance and other terms, and S represents the specific conductivity in bulk of the intermicellar fluid containing equicoagulating concentration of an electrolyte.

The results lead to the conclusion that a given rate of coagulation of uranyl ferrocyanide sol by different electrolytes is characterised by a definite value of the true ζ-potential, independent of the valency of the counter ions used. It has also been found that the difference in the values of true ζ-potential for the slow and rapid rates of coagulation is quite small. This indicates the existence of a critical zone of ζ-potential for the coagulation of the colloid.

The effect of dilution on the coagulation of uranyl ferrocyanide sol by electrolytes was studied by Dhar and Ghosh (*J. Phys. Chem.*, 1927, **31**, 187, 649). Mukherjee and coworkers (this *Journal*, 1936, **13**, 428) investigated the electrophoretic velocity of the sol in the presence of electrolytes and observed an increase in the mobility of the particles with lapse of time up to a certain point. It is probable that the increase in mobility with time in the presence of electrolytes results from the lowering of the effect of surface conductance with increase in the size of particles.

The present investigation was therefore undertaken to ascertain the effect of surface conductance on the apparent electrokinetic potential of the particles of uranyl ferrocyanide sol in the presence of equicoagulating concentrations of electrolytes containing counter ions of different valency.

The equation used for applying correction due to surface conductance is of the same form as discussed previously (Ghosh, this *Journal*, 1955, **32**, 69, 402 ; *Naturwiss.*, 1955, **42**, 121). It may be written as follows

$$\frac{1}{\zeta_a} = \frac{1}{\zeta} + m.\frac{1}{S} \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

in which ζ_a is the apparent value of the electrokinetic potential calculated from electro-osmotic data using Smoluchowski's equation, ζ, the true electrokinetic potential, S, the specific conductivity of the intermicellar fluid of the colloid-electrolyte mixture

and m represents $3V_1\chi/V_2R\zeta$ (where V_1 is the volume of the particles forming the diaphragm, V_2, the volume of the solution filling the diaphragm, χ, the specific surface conductance of the particles and R, their radius).

The equation for electrophoresis (Ghosh and Ray, *Nature*, 1955, **176**, 1080) is also of the same form as equation (1), but m, in it, stands for $\chi/R\zeta$ only.

The experimental details and the results are recorded below.

EXPERIMENTAL

Preparation of the Colloid.—Negatively charged uranyl ferrocyanide sol was prepared by a method similar to that of Mukherjee and coworkers (*loc. cit.*). Equal volumes of 0.1N uranyl nitrate and potassium ferrocyanide were mixed together. The precipitate of uranyl ferrocyanide, thus obtained, was washed by centrifuging with conductivity water. When the precipitate started to peptise, it was shaken with a very dilute solution of potassium ferrocyanide, centrifuged to separate bigger particles and dialysed for a week in cellophane bags. The sol was allowed to age for three weeks in a stoppered Jena bottle before use. Its uranyl ferrocyanide content and specific conductivity at 32° were 3.6 g./litre and 8.364×10^{-5} mhos respectively.

Determination of the Equicoagulating Concentration.—For rapid coagulation, an electrolyte solution (2 c.c.) was mixed with an equal volume of the colloid and the mixture was left as such for 10 minutes. After this period the mixture was centrifuged for 2 minutes at a definite speed. The supernatant solution was examined and the concentration of electrolyte, which just gave a clear supernatant solution, was taken as equicoagulating.

The determination of the equicoagulating concentration in the zone of slow coagulation was similar to that described above with this difference that the colloid-electrolyte mixture was allowed to stand undisturbed for 20 hours in place of 10 minutes.

Electro-osmotic Experiments

The electro-osmotic experiments were carried out at 32° by the Bredig's method in the U-tube apparatus, modified by Mukherjee *et al.* (*Nature*, 1922, **110**, 732). A definite volume of electrolyte solution was added to an equal volume of the colloid so that the final concentration of the electrolyte in the mixture represented its equicoagulating concentration. For experiments in the zone of rapid coagulation, this mixture was centrifuged after the expiry of 10 minutes, the supernatant liquid was decanted into a Jena bottle and the coagula were transferred with a small amount of the supernatant liquid into the U-tube.

The diaphragm was prepared in the U-tube by centrifuging at a given speed and the volume occupied by it was maintained constant in all the experiments so that V_1 and V_2 of equation (1) remained constant. R can also be assumed constant since the coagulation procedure was closely standardised. Centrifugate was used for supernatant liquid and its specific conductivity determined. The values of ζ_s were calculated from the velocity of electro-osmotic flow, current and specific conductivity, viscosity and dielectric constant, using Smoluchowski's equation.

TABLE I

Rapid coagulation.

$$\zeta = 23.7 \text{ m.v.} \quad m = \frac{3V_1}{V_2} \cdot \frac{\chi}{\zeta R} = 6\,315 \times 10^{-6}.$$

Electrolytes.	Equicoag. conc.	Sp. conducty. of supernat. soln at 32° ($S \times 10^6$).	Values of ζ_n (calc. from Smoluchowski's eq.).
NaCl	$5\,483 \times 10^{-3}N$	5.51 mhos	18.6 m.v.
$BaCl_2$	6.876×10^{-4}	1.56	11.9
$AlCl_3$	4.225×10^{-4}	1.36	11.3
NaCl & $BaCl_2$	1.185×10^{-3} & 4.035×10^{-4}	2.77	15.5
NaCl & $AlCl_3$	6.092×10^{-4} & 3.474×10^{-4}	2.06	14.6

For experiments in the zone of slow coagulation, the corresponding mixture of colloid and electrolyte was, however, centrifuged after the expiry of 20 hours for obtaining the coagula. ζ_n was measured by following the above procedure.

TABLE II

Slow coagulation.

$$\zeta = 25.1 \text{ m.v.} \quad m = \frac{3V_1}{V_2} \cdot \frac{\chi}{\zeta R} = 3.978 \times 10^{-6}.$$

Electrolyte.	Equicoag. conc.	Sp. conductv. of supernat. soln. at 32° ($S \times 10^4$).	Values of ζ_n (calc. from Smoluchowski eq.).
NaCl	$2.504 \times 10^{-3}N$	3.95 mhos	20.0 m v.
$BaCl_2$	5.480×10^{-4}	1.34	14.3
$AlCl_3$	3.750×10^{-4}	1.26	14.0
NaCl & $BaCl_2$	1.015×10^{-3} & 2.740×10^{-4}	2.34	18.0

Electrophoretic Experiments

These were carried out in a modified form of Burton's U-tube appratus using Ag/AgCl electrodes. This was fully described in a previous paper (Ghosh and De, this *Journal*, 1958, **35**, 837). The colloid electrolyte mixture was prepared by mixing equal volumes of sol and electrolyte solution of appropriate concentration, allowing

it to stand for 30 minutes and then centrifuging for 5 minutes at a slow speed to remove coarse particles. The clear supernatant liquid, filling the upper part of the limbs of the U-tube above the colloid-electrolyte mixture, was obtained by rapid centrifugation of the mixture of colloid and electrolytes of appropriate concentration after 20 hours of mixing. The potential gradient was found from the expression i/AS, where i represents the current ; A, the cross-sectional area of the limbs of the U-tube and S, the average of the specific conductances of the supernatant liquid and the colloid-electrolyte mixture. The values of ζ_a have been calculated from Smoluchowski's equation both for the upward and downward movements of the boundary. Their average values are recorded in Table III. The speed of the upward and downward moving boundaries agreed to within 9% on the average. The conductance of the supernatant solution was corrected for 33° since most of the experiments were performed at this temperature.

TABLE III

Slow coagulation.

$$\zeta = 25.5 \text{ m.v.} \quad m = \frac{X}{\zeta R} = 2.898 \times 10^{-6}.$$

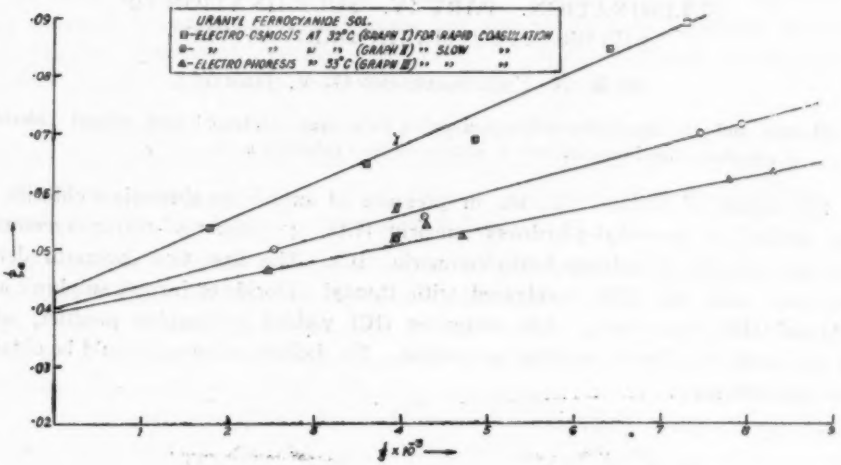
Electrolytes.	Equicoag. conc.	Sp. conductivity at 33° of Supernat. soln. ($S \times 10^4$).	Sp. conductivity at 33° of Colloid-electrolyte. ($K \times 10^4$).	ζ_a (calc. from Smoluchowski eq.).
NaCl	$2.504 \times 10^{-3} N$	4.08 mhos	4.03 mhos	21.6 m.v.
$BaCl_2$	5.480×10^{-4}	1.29	1.34	16.2
$AlCl_3$	3.750×10^{-4}	1.21	1.16	15.8
NaCl & $BaCl_2$	1.015×10^{-3} & 2.740×10^{-4}	2.28	2.27	18 5
NaCl & $AlCl_3$	7.446×10^{-4} & 2.400×10^{-4}	2.13	2.08	19 2

DISCUSSION

An examination of the electro-osmotic data presented in Tables I and II shows that ζ_a increases with the increase in S. When the reciprocals of ζ_a are plotted against the reciprocals of the corresponding S, a straight line is obtained (vide curves I and II of Fig. 1) as required by equation (1). This linear relationship indicates that at the equicoagulating concentrations of the electrolytes used, ζ and m, and consequently X, remain constant under the conditions of the experiment. The values of m for rapid and slow coagulations are found to be 6.315×10^{-6} and 3.978×10^{-6} respectively

and the corresponding values of true ζ-potentials are 23.7 m.v. and 25.1 m.v. respectively.

FIG 1



An examination of the electrophoretic data recorded in Table III shows that ζ_a increases with increase in S. A plot of $1/\zeta_a$ against $1/S$ (vide Curve III of Fig. 1) yields a straight line, as is to be expected from equation (1). This confirms the conclusion already drawn from the electro-osmotic data. The values of m and true ζ-potential are found to be 2.898×10^{-6} and 25.5 m.v. respectively.

For slow coagulation, the value of m of the electro-osmotic line (curve II, Fig. 1) is greater than that of the electrophoretic line (curve III, Fig. 1); therefore, when S is small, ζ_a found by electro-osmotic method is smaller than that found by the electrophoretic method for the same concentration of an electrolyte. Hence, the effect of surface conductance in depressing ζ_a is greater in electro-osmosis than in electrophoresis.

The value of ζ, found by the electro-osmotic and electrophoretic measurements, varies slightly, and so the average of these values 25.3 m.v., may be taken as the true ζ-potential of uranyl ferrocyanide sol in the presence of equicoagulating concentrations of the electrolytes used for slow coagulation. It may therefore be concluded that a given rate of coagulation of uranyl ferrocyanide sol is characterised by a definite value of the true ζ-potential, independent of the valency of the counter ions used.

It will also be noticed that the change in the value of true ζ-potential from relatively rapid to slow rate of coagulation is quite small (25.3 − 23 7 m.v.). In view of this fact it may be concluded that there is a critical zone of ζ-potential for coagulation of this sol by electrolytes.

PHYSICAL CHEMISTRY LABORATORIES,
UNIVERSITY COLLEGE OF SCIENCE
AND TECHNOLOGY, CALCUTTA-9.

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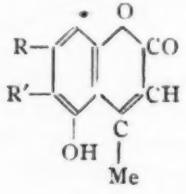
SULPHINATION. PART IV. SULPHINATION OF 5-HYDROXYCOUMARIN DERIVATIVES

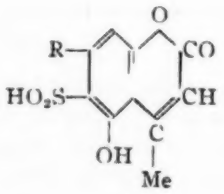
By R. N. Usgaonkar and G. V. Jadhav*

4-Methyl- and 4 : 7-dimethyl-5-hydroxycoumarins have been condensed with thionyl chloride in presence of anhydrous aluminium chloride to yield respective sulphinic acids.

The action of thionyl chloride in presence of anhydrous aluminium chloride has been studied on 4-methyl-5-hydroxycoumarin (IA), 4 : 7-dimethyl-5-hydroxycoumarin (IB) and 4 methyl-5-hydroxy-6-ethylcoumarin (IC). The first two coumarin derivatives, viz. (IA) and (IB), condensed with thionyl chloride to furnish sulphinic acids (IIA) and (IIB) respectively, while coumarin (IC) yielded a complex product, which did not melt but burnt, leaving a residue. No definite substance could be obtained from the complex.



(I)



(II)

[A : R = H ; R′ = H. B : R = Me ; R′ = H. C : R = H ; R′ = Et]

The constitution of the sulphinic acids (IIA & IIB) follows from the fact, that both of them exhibit coloration with alcoholic ferric chloride, showing $-SO_2H$ group to be in position-6, the only position *ortho* to hydroxyl group in the coumarin derivatives. The constitution of sulphinic acid (IIB) has been further confirmed by oxidation with hydrogen peroxide when it gives rise to the known 4 : 7-dimethyl-5-hydroxycoumarin-6 sulphonic acid, described by Merchant and Shah (this *Journal*, 1957, **34**, 47).

Experimental

4-Methyl-5-hydroxycoumarin-6-sulphinic Acid (IIA).—Ice-cold thionyl chloride (2.56 g , 1.6 c.c.) was gradually added to an intimate mixture of coumarin (IA, 2 g.) and powdered $AlCl_3$ (anhyd., 5.6 g.), cooled by surrounding the flask with ice. After keeping the mixture in ice for about half an hour, it was left at room temperature overnight and then decomposed by adding crushed ice and HCl. The whole mixture was left for about 5 hours at room temperature and in a refrigerator overnight. The solid was filtered, washed well and dried in vacuum. It was then triturated with liquor ammonia, diluted with water and insoluble residue was removed by filtration.

* Present address: D.E. Society's Bombay College, Dadar, Bombay-28.

The filtrate (dark coloured) was just acidified with HCl and flocculent precipitate separating was removed ; to the filtrate (now colorless) more HCl was added and it was left in the refrigerator, when sulphinic acid slowly separated as a white solid. It was dried in vacuum, m.p. 141-42° (decomp.), yield 0.5 g. Pure sulphinic acid was obtained by acidifying the aqueous solution of its ammonium salt (*vide infra*), m.p. 145-47° (decomp.). (Found : S, 12.80. $C_{10}H_8O_5S$ requires S, 13.33%). It exhibits a reddish violet coloration with alcoholic ferric chloride.

The *ammonium salt*, prepared by passing dry ammonia gas in the alcoholic solution of sulphinic acid (IIA), was crystallised from alcohol (diluted with few drops of water) in shining plates. It decomposes at 190° and then melts at about 240°. (Found : N, 5.27. $C_{10}H_{11}O_5NS$ requires N, 5.45%).

s-*Benzyliso*thiourea *derivative* was prepared by adding an aqueous solution of *s*-benzyl-*iso*thiourea hydrochloride to the solution of sodium salt of sulphinic acid, prepared by adding NaOH solution dropwise with stirring to the suspension of sulphinic acid in water, till a slight yellow coloration appeared in the solution (a little more of sulphinic acid was later added to it till coloration disappeared and the excess was removed by filtration). It was crystallised from dilute alcohol in thin needles, m.p. 145-47° (decomp.). (Found : N, 6.46. $C_{18}H_{18}O_5N_2S_2$ requires N, 6.89%).

4-*Methyl*-5-*hydroxycoumarin*-6-*sulphonic Acid* (*Sodium salt*).—Hydrogen peroxide (3 c.c. of 100 vol. + 10 c.c. of water) was added to the solution of sulphinic acid (IA, 0.4 g. in 5 c.c. of sodium bicarbonate solution) at room temperature and was left aside for about an hour and then heated on a water-bath for an hour. The resulting solution was acidified, concentrated to a small bulk, filtered from suspended impurities and poured in to a few c.c. of a saturated solution of common salt. The white sodium salt of sulphonic acid separating was filtered and dried.

s-*Benzyliso*thiourea *derivative* was prepared as usual from the sodium salt. It was crystallised from dilute alcohol, m.p. 183-85°. (Found : N, 6.54. $C_{18}H_{18}O_6N_2S_2$ requires N, 6.64%).

4 : 7-*Dimethyl*-5-*hydroxycoumarin*-6-*sulphinic Acid*.—Ice-cold thionyl chloride (1.6 c.c.) was gradually added to an intimate mixture of coumarin (IB, 2 g.) and powdered $AlCl_3$ (anhyd., 4.2 g.) and was kept on ice for about an hour and then left at room temperature overnight. It was then decomposed as usual by adding crushed ice and HCl, and the solid separating was washed and dried in vacuum. It was then suspended in water and NaOH solution was added to it dropwise with constant stirring till a permanent yellow tinge appeared in the solution. More of impure solid was added to it till the yellow colour disappeared. The insoluble portion was removed and to the clear filtrate HCl was added, when the solution turned milky. The sulphinic acid separated slowly from it, after scratching the walls of the container and keeping it in the refrigerator. It was dried in vacuum, m.p. 165° (decomp.), yield 1.2 g. Pure sulphinic acid was obtained by acidifying the aqueous solution of its pure ammonium salt, m.p. 165° (decomp.). (Found : S, 13.02. $C_{11}H_{10}O_5S$ requires S, 12.60%). It exhibits a reddish violet coloration with alcoholic ferric chloride.

Ammonium salt of (IIB) was prepared as before. It was crystallised from alcohol in shining plates, m.p. 212-14° (decomp.). (Found: N, 5.40. $C_{11}H_{13}O_5NS$ requires N, 5.16%).

s-*Benzylisothiourea derivative of* (IIB) was prepared as in the previous case. It was crystallised from alcohol in glistening rhombic plates, m.p. 171-73° (decomp.). (Found: N, 7.01. $C_{19}H_{20}O_5N_2S_2$ requires N, 6.67%).

4:7-*Dimethyl-5-hydroxycoumarin-6-sulphonic Acid* (*Sodium salt*).—The sulphinic acid (IIB) was oxidised by adding hydrogen peroxide, following the same procedure as that of oxidation of (IIA), and the sulphonic acid was isolated as its sodium salt.

s-*Benzylisothiourea derivative* was prepared as usual from the sodium salt. It was crystallised from alcohol in glistening prisms, m.p. 183-84°. The mixed m.p. with the authentic specimen of the same derivative of the same sulphonic acid, prepared according to Merchant and Shah (*loc. cit.*), showed no lowering.

4:7-*Dimethyl-5-hydroxycoumarin-6-ethylsulphone*.—To the alcoholic solution of sulphinic acid (1 g.), an EtOH-KOH solution was added with constant stirring till a slight permanent yellow tinge appeared in the solution (white potassium salt separated). A little more of sulphinic acid was then added to it till the colour disappeared and then it was refluxed with the addition of water (3 c.c.) and ethyl iodide (0.8 c.c.) for 18 hours. Some solid separated from the boiling mixture. It was filtered hot and the filtrate was kept in a refrigerator from which the sulphone crystallised out. It was boiled with water to remove impurities and then crystallised from alcohol in thin needles, m.p. 194-95°. (Found: S, 11.25. $C_{13}H_{14}O_5S$ requires S, 11.34%).

The solid that was obtained from the boiling mixture was found mainly to be 4:7-dimethyl-5-hydroxycoumarin (IA), contaminated with a small amount of another substance, m.p. 270° (decomp.). The coumarin was separated by extracting it with alcohol as the latter substance was insoluble in most of the organic solvents. (This substance was not investigated).

4:7-*Dimethyl-5-hydroxy-6-chloromercuricoumarin*.—To the solution of sulphinic acid (IIB, 0.5 g. in 10 c.c. of absolute alcohol) an alcoholic solution of mercuric chloride (0.5 g. in 5 c.c.) was added and the solution was well shaken and kept aside for 7-8 hours at room temperature. A crystalline substance slowly separated with continuous evolution of sulphur dioxide. The solid was filtered, first boiled with water and then with alcohol, m.p. above 270°. (It was purified in this way as it could not be crystallised). (Found: Hg, 46.6. $C_{11}H_9O_3HgCl$ requires Hg, 47.1%). It dissolves in sodium hydroxide solution with a deep yellow colour.

ORGANIC CHEMISTRY LABORATORIES,
THE INSTITUTE OF SCIENCE,
BOMBAY.

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ESTIMATION OF PALLADIUM BY αβ-DIOXIMINO-ACETOACETANILIDE

By J. S. Dave and A. M. Talati

αβ-Dioximino-acetoacetanilide precipitates palladium quantitatively as $Pd(C_{10}H_{10}O_3N_3)_2$. The gravimetric estimation of palladium by this reagent has been investigated and the effects of *p*H, anions and cations on the estimation have been studied.

The dioximes are widely used in the separation and estimation of palladium. Dimethylglyoxime (Wunder and Thuringer, *Chem. Z.*, 1912, **36**, 550 ; *Z. anal. Chem.*, 1913, **52**, 101, 660, 740) has now practically superceded all other reagents for the estimation of palladium gravimetrically. Methylbenzoylglyoxime (Grisollet and Serivgne, *Chem. Abst.*, 1931, **25**, 261 ; Hanus *et al.*, *Chem. News*, 1925, **131**, 401 ; 1926, **132**, 1) and oxalene-diamidoxime (Das Gupta, this *Journal*, 1953, **30**, 761) have also been proved fruitful in the separation and determination of palladium.

As a part of our investigation on the oximes of acetoacetamides, we investigated the applicability of αβ-dioximes, obtained from the amides, to the analysis of palladium. We have observed that palladium is quantitatively precipitated by αβ-dioximino-acetoacet (aryl) amide. The separation and determination of palladium by αβ-dioximino-acetoacetanilide have been discussed in the present communication. Palladium forms a yellow complex, having the formula $Pd(C_{10}H_{10}O_3N_3)_2$, with αβ-dioximino-acetoacetanilide. Palladium is quantitatively precipitated from fairly acidic solutions (*p*H 0.4) under which conditions no other metal complex of this reagent is precipitated. Mercury, tin, cobalt, nickel, zinc, cadmium, copper, manganese, calcium, barium, magnesium, iron (Fe^{III}) and chromium do not interfere under the experimental conditions. It has been observed, however, that an error is introduced when nitrate, cyanide or iodide is present and the estimation is carried out under the same conditions.

Experimental

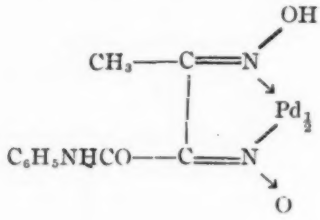
αβ-Dioximino-acetoacetanilide was prepared from acetoacetanilide (Dave and Talati, *Curr. Sci.*, 1957, **26**, 326) and a 1% alcoholic solution of this reagent was used in all the estimations.

A weighed quantity of palladous chloride was dissolved in a little warm HCl (conc.) and was then diluted with water to a definite volume. Palladium content of the solution was determined by the dimethylglyoxime method. The reagents used were of C. P. grade.

Composition of the Complex.—Palladium chloride solution (10 c.c.) was diluted to about 100 c.c. with distilled water, acidified with HCl (dil.), and to the warm solution was added a sufficient amount of the reagent solution. Yellow precipitates appeared, which were digested on the water-bath for about an hour. The flocculent precipitate was filtered, washed with water and alcohol and dried at 110-20°. A weighed

quantity of the Pd-complex was taken in a crucible and its Pd content was estimated by the ignition method. [Found : Pd, 19.15, 19.48, 19.55. Calc. for $Pd(C_{10}H_{10}O_3N_3)_2$: Pd, 19.50%].

The results suggest the composition as $Pd(C_{10}H_{10}O_3N_3)_2$ for the palladium complex of $\alpha\beta$-dioximino-acetoacetanilide, which may be represented as :



Procedure.—Palladium was precipitated from the solution as described above. The precipitate was filtered through a quantitative filter paper or a sintered glass crucible, washed with water and dried at 110-20° to a constant weight. It was weighed as $Pd(C_{10}H_{10}O_3N_3)_2$, the factor for palladium being 0.1950. Some of the results are recorded in Table I.

TABLE I

Pd taken.	Pd-complex.	Pd found.	Error.
5.87 mg.	30.1 mg.	5.87 mg.	± 0.00
8.62	44.4	8.66	+ 0.04
11.40	58.3	11.37	− 0.03
22.80	117.0	22.82	+ 0.02

Effect of pH.—In order to study the *p*H range over which palladium could be completely precipitated by this reagent, estimation of palladium was carried out in solutions having different *p*H values. The *p*H values of the undiluted filtrates were determined by an L & N *p*H meter (No. 7664). The results, recorded in Table II, show that palladium is completely precipitated by this reagent above *p*H 0.1 (and at least up to *p*H 8.86).

TABLE II

Pd taken.	*p*H.	Pd-complex.	Pd found.
11.40 mg.	0.08	58.3 mg.	11.37 mg.
8.62	0.40	44.2	8.62
8.62	0.70	44.4	8.66
5.87	1.90	30.1	5.87
8.62	8.86	44.6	8.72

Effect of Anions.—The estimation of palladium was carried out in presence of different anions. The results are recorded in Table III. It was found that at *p*H 0.4 to 0.7, no precipitate was obtained in presence of potassium iodide ; low results with potassium cyanide and high results with sodium nitrate were obtained. No

interference was caused by sodium acetate, tartaric acid or potassium sulphate, when the estimation was carried out from acidic solutions; similarly potassium iodide and potassium bromide caused no interference when the estimation was carried out from neutral or alkaline solutions.

TABLE III

Pd taken.	*p*H.	Salt/acid added.		Pd-complex	Pd found.	Error.
8.62 mg.	0.4-0.7	Na-acetate	2.0 g.	44.4 mg.	8.66 mg.	+ 0.04 mg.
8.62	,,	$NaNO_3$	2.0	48.1	9.38	+ 0.78
8.62	,,	KI	2.0	...	...	...
8.62	,,	Tartaric acid	2.0	43.7	8.52	− 0.10
8.62	,,	KCN	0.06	31.1	6.06	− 2.52
11.40	2.40	K_2SO_4	2.0	58.6	11.43	+ 0.03
11.40	7.38	KBr	2.0	59.0	11.51	+ 0.11
11.40	7.78	KI	2.0	58.5	11.41	+ 0.01

Estimation of Palladium in presence of Cations.—Palladium can be estimated in presence of a large number of metal ions at *p*H 0.4 to 0.7 by following the same procedure (the precipitates are twice washed with dil. HCl solution and then with water). The results, shown in Table IV, show that the metals under investigation cause little or no interference.

TABLE IVA

Pd taken = 8.62 mg.

Salts added.		Pd-complex.	Pd found.	Error.
$CdSO_4$	0.064 g	44.2 mg.	8.62 g.	± 0.00 mg.
$SnCl_2$	0.113	44.6	8.70	+ 0.08
$CrCl_3$	0.134	44.9	8.75	+ 0.13
$ZnSO_4$	0.072	44.9	8.75	+ 0.13
$MnCl_2$	0.099	44.0	8.58	− 0.04
$CoCl_2$	0.119	44.4	8.66	+ 0.04
$FeCl_3$	0.135	44.1	8.60	− 0.02
$CaCl_2$	1.100	44.0	8.58	− 0.04
$BaCl_2$	1.500	44.0	8.58	− 0.04
$MgCl_2$	0.500	43.8	8.54	− 0.08
$HgCl_2$	0.136	44.6	8.70	+ 0.08

TABLE IVB

Pd taken = 5.87 mg.

Ni added.	Cu added.	Pd-complex.	Pd found.	Error.
6.81 mg.	...	30.4 mg.	5.93 mg.	+ 0.06 mg.
13.22	...	30.4	5.93	+ 0.06
...	7.85 mg.	30.5	5.95	+ 0.08
...	15.25	30.8	6.01	+ 0.14

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CHEMISTRY DEPARTMENT,
FACULTY OF SCIENCE
AND
TEXTILE CHEMISTRY DEPARTMENT,
FACULTY OF TECHNOLOGY AND ENGINEERING,
M.S. UNIVERSITY OF BARODA,
BARODA.

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BENZOYL CHLORIDE AS A POLAR SOLVENT. PART IV. SOLVOLYTIC REACTIONS IN BENZOYL CHLORIDE

By Ram Chand Paul, Malkiat Singh Bains and Gurdev Singh

Solvolysis of a large number of oxides, nitrates, nitrites, oxalates, carbonates, acetates, sulphites and sulphides has been studied quantitatively in benzoyl chloride, and a mechanism for these solvolytic reactions, based on the ionisatio n of benzoyl chloride, has been proposed.

A few solvolytic reactions have already been studied in benzoyl chloride in order to prepare some of the benzoyl compounds (Oakwood and Weisgerber, "Org. Syntheses", 1944, Vol. 24, p. 14 ; Nef, *Annalen*, 1895, **287**, 307 ; Sonntag, *Chem Rev.*, 1953, **52**, 340 ; McGookin and Page, *J. Chem. Soc.*, 1951, 2769 ; Francis, *Ber.*, 1906, **39**, 3798). Benzoic anhydride and dibenzoyl sulphide have been prepared by solvolysing silver, lead (Lachowicz, *Ber.*, 1884, **17**, 1281) and potassium nitrates (Diels and Okada, *Ber*, 1911, **44**, 3335) and sodium sulphide (Fromm and Schmoldt, *Ber.*, 1907, **40**, 2862) respectively with benzoyl chloride.

In the present investigation, the solvolytic action of benzoyl chloride has been studied on oxides and other salts. In most of the cases, the anhydrous chlorides are insoluble in benzoyl chloride and, thus, this affords a very good method for their preparation. The results of these observations are recorded in Table I. The percentage conversion in this table means percentage of the metal chloride or its compound present in the product isolated.

The solvolysis of cupric and zinc oxides proceeds very slowly at room temperature (30°) and intermediates of the composition $3CuCl_2.CuO.C_6H_5COCl$ and $2ZnCl_2.3(ZnO.2C_6H_5COCl)$ have been isolated. On refluxing the reactants, however, the reaction becomes quite brisk and almost pure cupric and zinc chlorides are formed.

The products of solvolysis of mercuric oxide, lead oxide and selenium dioxide are also pure chlorides. In the case of mercuric oxide and selenium dioxide, the conversion to chloride is quite rapid, but lead oxide takes a very long time (140 hours). The solvolysis of cadmium and calcium oxides is also very slow and increases with time. Aluminium, chromium and nickelic oxides, and titanium dioxide have been found to be reluctant to solvolyse.

Bismuth oxychloride on being acted upon benzoyl chloride affords a compound $BiCl_3.(C_6H_5CO)_2O$ which can alternatively be represented as $BiOCl.2C_6H_5COCl$. The structure of this compound has been confirmed by allowing it to react with pyridine in benzoyl chloride, when a complex of the composition $(C_5H_5N.C_6H_5CO)_3.BiCl_6$ is formed. Only the formula $BiCl_3.(C_6H_5CO)_2O$ can give rise to this complex as $BiCl_3$ is known to be a Lewis acid (Dermer *et al.*, *J. Amer. Chem. Soc.*, 1941, **63**, 2881). Moreover, bismuth oxychloride can only act as a base in benzoyl chloride and will not form any compound with pyridine in this solvent.

Bismuth trioxide forms a compound of the composition $2BiCl_3.3(C_6H_5CO)_2O$ in benzoyl chloride and its composition has been confirmed by the synthesis from benzoic anhydride and bismuth trichoride in benzoyl chloride.

Antimony oxychloride or antimony trioxide reacts with benzoyl chloride to form $SbCl_3.(C_6H_5CO)_2O$. The structure of this compound has been confirmed by allowing antimony trichloride to react with benzoic anhydride in benzoyl chloride, when the same compound is obtained.

The solvolysis of silver nitrate, which was studied qualitatively (*loc. cit.*), has been repeated and an almost complete conversion to silver chloride has been observed. Sodium nitrate, sodium nitrite, potassium oxalate, mercuric acetate and cadmium carbonate are also solvolysed to form the corresponding chlorides. The solvolysis of potassium sulphite is very slow and increases with lapse of time. After refluxing for 40 hours, the conversion to chloride has been found to be only about 37 %. The conversion of cadmium sulphide to cadmium chloride is complete, but the final product is slightly contaminated with some inert substances.

Koehl and Wenzke (*J. Amer. Chem. Soc.*, 1937, **59**, 1418) have suggested the existence of $(C_6H_5CO)^+Cl^-$ as one of the resonating forms contributing to the stable structure of benzoyl chloride. This view is also supported by the low value of the dissociation energy of the benzoyl-chlorine bond (73.1 Kcal.) in benzoyl chloride molecule (Carson *et al.*, *J. Chem. Soc.*, 1950, 656) as compared to that of the phenyl-chlorine bond (85.6 Kcal.) in chlorobenzene (Szware and Williams, *J. Chem. Phys.*, 1952, **20**, 1171). The work of Burton and Praill (*J. Chem. Soc.*, 1951, 529) also provides a proof of the existence of benzoylium ions. In the light of these observations, the ionisation of benzoyl chloride is presumed to be as follows:

$$C_6H_5COCl \rightleftharpoons C_6H_5CO^+ + Cl^-$$

Assuming these salts to be feebly soluble and slightly ionised, the mechanism of these solvolytic reactions in benzoyl chloride can be explained on the basis of the ionisation of benzoyl chloride, given above. Thus, the solvolysis of silver nitrate can be represented as:

$$C_6H_5COCl \rightleftharpoons C_6H_5CO^+ + Cl^-$$
$$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$$
$$Ag^+ + NO_3^- + C_6H_5CO^+ + Cl^- \longrightarrow AgCl + C_6H_5CONO_3.$$

Benzoyl nitrate formed in this reaction may decompose to furnish the oxides of nitrogen or react with excess of benzoyl chloride, yielding nitrosyl chloride and chlorine (Diels and Okada, *loc. cit.*) as under:

$$4C_6H_5CONO_3 \longrightarrow 2(C_6H_5CO)_2O + 4NO_2 + O_2$$
$$C_6H_5CONO_3 + 3C_6H_5COCl \longrightarrow 2(C_6H_5CO)_2O + NOCl + Cl_2.$$

Similarly, the solvolysis of oxalates, nitrites, carbonates and sulphites, when benzoyl oxalate, benzoyl nitrite, benzoyl carbonate and benzoyl sulphite are formed, can be explained on the basis of the proposed ionisation of benzoyl chloride. These

benzoyl compounds, however, are unstable and decompose further to afford carbon dioxide and monoxide, oxides of nitrogen, carbon dioxide and sulphur dioxide, respectively :

$$Cd^{2+} + CO_3^{2-} + 2C_6H_5CO^+ + 2Cl^- \rightarrow CdCl_2 + (C_6H_5CO)_2CO_3$$
$$(C_6H_5CO)_2CO_3 \rightarrow (C_6H_5CO)_2O + CO_2.$$

Mercuric acetate gives mercuric chloride along with acetic anhydride and benzoic anhydride,

$$Hg^{2+} + 2CH_3COO^- + 2C_6H_5CO^+ + 2Cl^- \rightarrow HgCl_2 + (C_6H_5CO)_2O + (CH_3CO)_2O.$$

Cadmium sulphide reacts with benzoyl chloride to yield dibenzoyl sulphide :

$$Cd^{2+} + S^{2-} + 2C_6H_5CO^+ + 2Cl^- \rightarrow CdCl_2 + (C_6H_5CO)_2S.$$

In the case of the solvolysis of oxides, it has been assumed by McGookin and Page (*loc. cit.*) that the first stage of the reaction is the formation of an addition compound between the oxide and the acid chloride, which undergoes an isomeric change to give rise to an addition compound of the metal chloride and acid anhydride. This additon compound may further decompose to furnish the metal chloride and acid anhydride ; the latter being soluble in benzoyl chloride goes into solution :

$$HgO + 2C_6H_5COCl \rightarrow HgO.2C_6H_5COCl \rightarrow HgCl_2.(C_6H_5CO)_2O \rightarrow HgCl_2 + (C_6H_5CO)_2O.$$

The isolation of the intermediates, already mentioned in connection with the solvolysis of zinc and cupric oxide, supports this view. In the case of the trioxide and the oxychlorides of antimony and bismuth, the benzoic anhydride formed remains attached to the metal chloride.

Experimental

Benzoyl chloride used was purified as described in Part I (this *Journal*, 1958, **35**, 489). All manipulations were carried out in a dry box and carefully dried anhydrous substances, the purity of which was established by analysis, were used.

Procedure.—Partial solvolysis of some of the compounds could be brought about at room temperature (30°) by thoroughly mixing the compounds with benzoyl chloride in sealed ampoules. To obtain complete or maximum solvolysis, well-dried solid compound (2-4 g.) was added to benzoyl chloride (30-40 c.c.) in a 100 c.c. standard-joint flask equipped with an air condenser and calcium chloride guard-tube. The reaction mixture was refluxed for a time, varying from a few minutes to many days, depending upon the speed of the reaction. Benzoyl chloride was replenished occasionally. The product was filtered, washed with dry petroleum ether (b.p. 40-60°), dried in vacuum and analysed. In some cases, the solvolysed product went into solution, and it was isolated by the addition of an inert solvent like dry petroleum ether and CCl_4 or by chiling the solution in ice. The results are recorded in Table I.

TABLE I

Compound.	Solvolysed product.	Solv. temp.	Time.	Found.	Calc.	%Solvolysis.
CuO	$3CuCl_2.CuO.C_6H_5COCl$	30°	48 hrs.	Cu : 40.48 Cl : 39.85	40.85 39.92	100
*CuO	$CuCl_2$	150-60°	3	Cu : 46.28 Cl : 51.75	47.21 52.79	100
ZnO	$2ZnCl_2.3(ZnO.2C_6H_5COCl)$	30°	48	Zn : 23.70 Cl : 25.85	24.00 26.15	
*ZnO	$ZnCl_2$	Reflux	3	Zn : 45.50 Cl : 49.45	47.80 52.20	100
HgO	$HgCl_2$	,,	3	Hg : 73.75 Cl : 26.38	73.80 26.20	
*SeO_2	$SeCl_4$	,,	¼	Se : 32.85 Cl : 58.40	35.75 64.25	100
PbO	$PbCl_2$	,,	140	Pb : 74.50 Cl : 25.12	74.47 25.53	100
CdO	$CdCl_2$ + CdO	,,	30	Cd : 61.82 Cl : 25.34	... ...	100
CaO	$CaCl_2$ + CaO	,,	55	Ca : 47.61 Cl : 26 91	... ...	100
Sb_2O_3	$SbCl_3.(C_6H_5CO)_2O$	,,	¼	Sb : 27.11 Cl : 23.61	26.81 23.45	100
Bi_2O_3	$2BiCl_3.3(C_6H_5CO)_2O$	30°	48	Bi : 30.81 Cl : 16.13	31.94 16.28	100
SbOCl	$SbCl_3.(C_6H_5CO)_2O$	Reflux	½	Sb : 26.76 Cl : 23.61	26.81 23.45	100
BiOCl	$BiCl_3.(C_6H_5CO)_2O$	30°	48	Bi : 39.20 Cl : 18.99	38.60 19.67	100
$NaNO_3$	NaCl	Reflux	4	Cl : 60.83	60.68	100
$AgNO_3$	AgCl	,,	6	Ag : 74.89	75.22	100
$NaNO_2$	NaCl	,,	3	Cl : 60.02	60.68	100
*$(CH_3COO)_2Hg$	$HgCl_2$	150°	5	Hg : 73.50 Cl : 25.80	73.80 26.20	100
*$CdCO_3$	$CdCl_2$	Reflux	12	Cd : 58.50 Cl : 37.04	61.38 38.62	100
*CdS	$CdCl_2$	,,	4	Cd : 55.36 Cl : 34.03	61 38 38.62	100
$(COOK)_2$	KCl	,,	15	Cl : 46.60	46.99	100
K_2SO_3	KCl + K_2SO_3	,,	40	Cl : 17.76		37.19

In the compounds marked by an asterisk (*), the metal/chlorine ratio of the product of solvolysis agrees with the one required for the corresponding chloride, but lower results for metal and chlorine in analysis show that the product is contaminated with some inert substance.

Solvolysis of Bismuth Oxychloride.—Bismuth oxychloride on treating with benzoyl chloride furnishes a compound which can be represented either as $BiCl_3.(C_6H_5CO)_2O$ or as $BiOCl.2C_6H_5COCl$. To determine the structure of this compound, its solution (1.8 g.) in benzoyl chloride (50 c.c.) was treated with pyridine (0.8 g.) in the same solvent (20 c.c.). The mixture was warmed, triturated and allowed to stand for half an hour. A white product separated which was filtered, washed with dry petroleum ether and kept under vacuum to afford $(C_5H_5N.C_6H_5CO)_3.BiCl_6$, yield 1.8 g. [Found: Cl, 22.05; Bi, 21.31; pyridine, 23.20. $(C_5H_5N.C_6H_5CO)_3BiCl_6$ requires Cl, 21.87; Bi, 21.50; pyridine, 24.30%).

The product is white in colour and melts at 230° with decomposition. Pyridine was estimated according to the Jackson and Smith method (*J. Amer. Chem. Soc.*, 1940, **62**, 544).

Reaction of Bismuth Trichloride with Benzoic Anhydride.—Bismuth trioxide, on treatment with benzoyl chloride, yields a compound $2BiCl_3.3(C_6H_5CO)_2O$ (m.p. 162-63°), which can alternatively be represented as $Bi_2O_3.6C_6H_5COCl$. To confirm the structure of this compound, bismuth trichloride (1 g. in 50 c.c. benzoyl chloride) was treated with benzoic anhydride (1.2 g. in 25 c.c. benzoyl chloride). The reaction mixture was warmed to 60-70° and allowed to stand for 2 hours. A white product separated out, which was filtered, washed with dry petroleum ether and dried in vacuum to yield $2BiCl_3.3(C_6H_5CO)_2O$, (1.5 g.), m.p. 163-64 . [Found : Cl, 16.53; Bi, 30.95. $2BiCl_3.3(C_6H_5CO)_2O$ requires Cl, 16.28; Bi, 31.94%].

Reaction of Antimony Trichloride with Benzoic Anhydride.—The compound of antimony oxychloride or antimony trioxide with benzoyl chloride (m.p. 71-72°) can be represented either as $SbCl_3.(C_6H_5CO)_2O$ or $SbOCl.2C_6H_5COCl$. To decide its structure, the solutions of antimony trichloride (1 g. in 10 c.c. benzoyl chloride) and benzoic anhydride (1 g. in 20 c c. benzoyl chloride) were mixed. After warming the mixture for a few minutes, the solution was allowed to cool, when fine dirty white crystals separated, which were filtered, washed with dry petroleum ether and kept under vacuum to give $SbCl_2.(C_6H_5CO)_2O$, yield 1 g. [Found : Cl, 23.31 ; Sb, 25.95. $SbCl_3.(C_6H_5CO)_2O$ requires Cl, 23.45 ; Sb, 26.81%].

CHEMISTRY DEPARTMENT,
PANJAB UNIVERSITY,
HOSHIARPUR.

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VISCOSITY OF SUPERSATURATED SOLUTIONS OF SOME IONIC CRYSTALS. PART II

D. Sri Rama Rao

Measurements of viscosity of supersaturated solutions of hydrated $MgSO_4$, $ZnSO_4$, $CoSO_4$, $NiSO_4$, $Ni(NO_3)_2$ and $CoCl_2$ have been made. The viscosity curves, as far as traced below the transition temperatures, remain perfectly regular and there is nothing to indicate any change in the constitution of the solutions. Supersaturated solutions, as such, show no abnormal properties, as compared with ordinary solutions.

The present investigation was undertaken with a view to measuring the viscosities of supersaturated solutions of hydrated salts, capable of existing in different degrees of hydration, in temperature regions on either side of transition points. Saturated solutions were prepared above the transition temperature (where the lower hydrates exist) and viscosity measurements were made particularly on either side of the transition point. It has been observed that the viscosity curves, as far as these have been traced above and below the transition temperatures, remain quite continuous. We are thus justified in concluding that the solute in a supersaturated solution undergoes no sudden change in the constitution in passing through the transition temperatures, as judged by viscosity measurements. De Coppet (*Compt. rend.*, 1871, **73**, 1324) found that the depression of freezing point in supersaturated solutions varied continuously with concentration even beyond the point of saturation. Chatterji and Gopal (this *Journal*, 1942, **19**, 55) found no change in the coefficient of expansion in passing through the point of supersaturation. It would therefore appear that supersaturated solutions,as such, show no sudden variation in properties at transition temperatures.

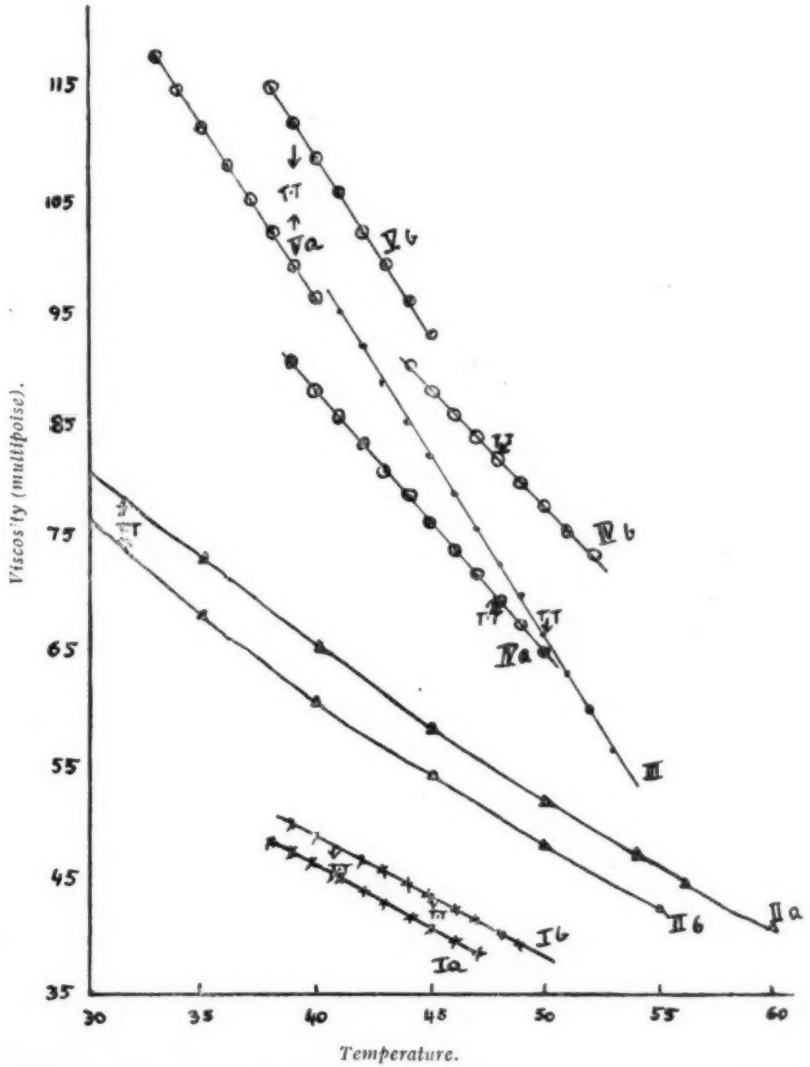
There was no sign of spontaneous crystallisation in the cases examined in this work even when the temperature was lowered 25° to 30° below saturation temperature, and kept for several hours at such lowered temperatures. Crystallisation, however, occurred immediately on inoculating the solutions with minute crystals of solutes.

Experimental

The apparatus used and the method adopted for measuring the viscosity of the solutions were the same as recorded in the previous paper (this *Journal*, 1956, **33**, 171). Viscosities of supersaturated solutions of hydrated $MgSO_4$, $ZnSO_4$, $CoSO_4$, $NiSO_4$, $Ni(NO_3)_2$ and $CoCl_2$ were measured. Since these salts were very viscous at low temperatures, a viscometer with a capillary of suitable radius was used. The solution to be examined was kept stirred at a constant temperature for a sufficiently long time, varying from 2 to 3 hours. By applying suction this solution was filtered through a sintered crucible directly into the experimental tube. After allowing sufficient time for the liquid to attain the temperature of the bath, readings were taken.

In order to obtain the solubilities of the salts, a small quantity of the saturated solution after the experiment was transferred to a small weighed dish, evaporated and heated to a constant weight. The weights obtained agree very well with the data recorded in the Chemical Engineer's Handbook (1950) and Physico-Chemical Tables (Castell-Evans, 1911).

FIG. 1



Ia Soln.	50.10% $CoSO_4$	Ib	Soln.	51.80% $CoSO_4$	IIa	Soln.	60.42% $NiSO_4$
IIb ,,	57.40% $NiSO_4$	III	,,	48.00% $CoCl_2$	IVa	,,	50.30% $MgSO_4$
IVb ,,	51.77% $MgSO_4$	Va	,,	70.31% $ZnSO_4$	Vb	,,	72.00% $ZnSO_4$

The results are plotted in Fig. 1, which is self-explanatory. When the viscosities of supersaturated solutions are plotted against their temperatures, curves similar to those shown in the previous paper (*loc.cit.*) are obtained.

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CHEMISTRY DEPARTMENT,
PACHAIYAPPA'S COLLEGE,
MADRAS-30.

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INTERACTION OF CLAYS WITH ELECTROLYTES: CHANGES IN SEDIMENTATION VOLUME IN PRESENCE OF CETYL TRIMETHYLAMMONIUM BROMIDE

By M. Adhikari

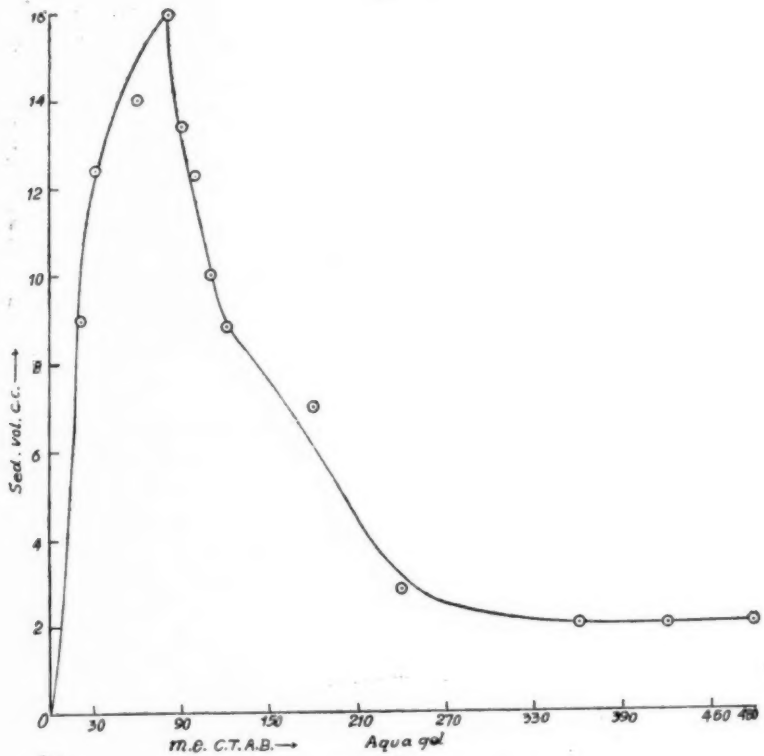
A study of the changes in sedimentation volume of different H-clay minerals in presence of cetyl trimethylammonium bromide has been made and it has been proved that when the curves of sedimentation volume *vs.* concentration of cetyl trimethylammonium bromide are compared, then at any particular concentration of cetyl trimethylammoium bromide (as also of the clay), the following sequence of sedimentation volume is observed: montmorillonite > vermiculite > illite > kaolinite, and the sedimentation volumes of all soil clays, which are predominantly illitic in nature containing traces of kaolinite in them, fall in line with vermiculite and illite.

That certain organic compounds of montmorillonite have the property of swelling and dispersing in organic liquids, has been studied in great detail by Jordon (*Min. Mag.*, 1949, **29**, 598). From the study of the gel volume of a series of normal primary aliphatic amine-montmorillonite complex in nitrobenzene, benzene and *iso*amyl alcohol, he has shown that organophilic properties are negligible until an amine with a chain of 10 carbon atoms is reached and that 12 carbon atoms are required for maximum swelling. The dispersive action of the organic complex is shown most prominently in polar solvents like nitrobenzene. The organophilic character is also developed in the complex formed by montmorillonite with quaternary ammonium salts having long aliphatic chains, as has been shown by Jordon (*loc cit.*). Mukherjee (this *Journal*, 1956, **33**, 749) from the study of the hydration and swelling characteristics of certain organic (e.g., protein, brucine, diethylamine, cetyl trimethylammonium bromide etc.) complexes of montmorillonite, has shown that in the case of clay complexes with brucine, diethylamine etc., the hydrophilic character is reduced, but the products do not become noticeably organophilic except in the case of cetyl trimethylammonium bromide-treated clay.

Chakravarti (*Science & Culture*, 1956, **22**, 170) has studied the effect of addition of a few quaternary ammonium complexes to aqueous suspensions of H-montmorillonite and H-kaolinite and their mixtures with particular reference to the sedimentation volume and ζ-potential. He has shown that the sedimentation volume attains a maximum value at a certain concentration of the added quaternary compounds which correspond to an amount equivalent to 75–80% of the b.e.c. of the clay. The ascending portion of the curves corresponds to the gradual replacement of H^+ ions by the large organic cations and a simultaneous diminution of the ζ-potential caused by a suppression of the ionic atmosphere. The descending portion of the curves corresponds to charge reversal,

as shown by ζ-potential measurements. Consequently deflocculation occurs in place of flocculation which attains in the ascending portion of the curves. These variations are so prominent that Chakravarti (*loc. cit.*) has suggested the utilisation of sedimentation and ζ-potential measurements for determining the proportion of a binary mixture of

FIG. 1



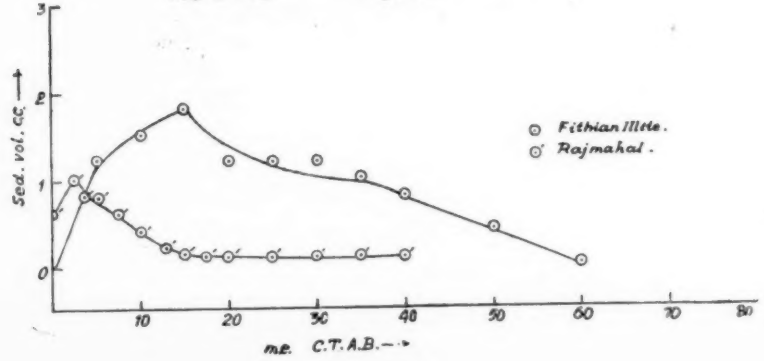


FIG. 2

montomorillonite and kaolinite clays. The present paper deals with the studies of the effect of addition of cetyl trimethylammonium bromide to aqueous suspensions of H-clays with particular reference to the sedimentation volume, because preliminary experiments actually indicated significant variations of this property (Chakravarti, *loc cit*).

FIG. 3

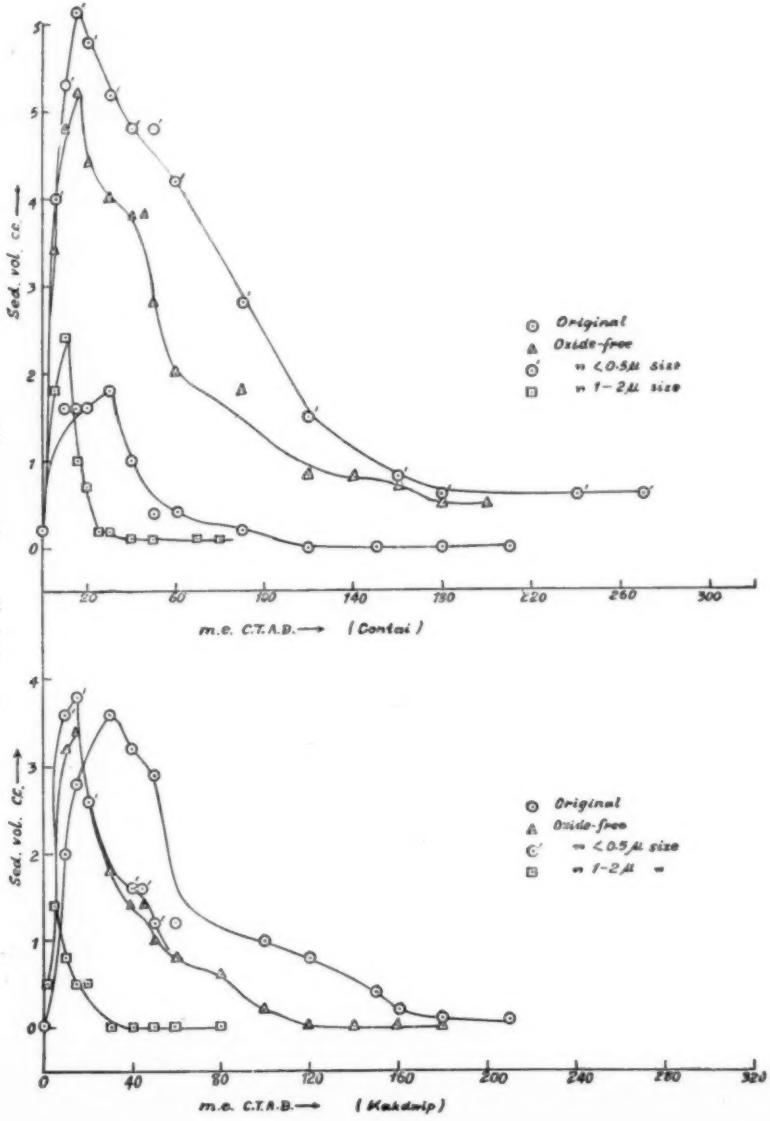


FIG. 4

Experimental

Hydrogen clays from (1) aqua-gel, (2) Rajmahal kaolin, (3) & (4) Malavangatta and Bagespura vermiculites and surface soils of West Bengal from the following localites- (5) Kakdwip (24 Parganas), (6) Contai (Midnapore), (7) Burdwan, (8) Suri (Birbhum), and (9) Maynaguri (Jalpaiguri)- were prepared by the usual procedure. The clay mineral content of samples No. (1) and (2) are montmorillonite and kaolinite respectively, as has been found from X-ray and differential thermal analyses (Adhikari, unpublished). Samples No. (3) and (4) are vermiculites and soil samples are predominantly illitic in nature with traces of kaolinite in them which have been shown earlier (Adhikari & Ray, *Science & Culture*, 1957, **23**, 258 ; Adhikari, *J. Indian Soc. Soil Sci.*, 1957, **5**, 199 ; *Indian J. Appl. Chem.*, 1958, **21**, 149). The removal of free oxides from the soil clays was carried out according to the method of Marshall and Jeffries (*Proc. Soil Sci. Amer.*, 1945, **10**, 1397). The solution of cetyl trimethylammonium bromide was prepared from vacuum-dry samples and standardised by conductometric titration of the bromide with $AgNO_3$ solution.

In a series of graduated well-stoppered cylinders of equal dimensions were taken the well dispersed H-clays (0.4% conc., 10 c c. each) and gradually increasing amounts of $N/40$ cetyl trimethylammonium bromide (C.T.A.B.) were added ; the final volume was made up with water to 20 c.c. (0.2% clay concentration finally). After mixing well, the cylinders were left for 24 hours and the sedimentation volume was recorded.

The results of the individual clays are shown in Figs 1-6 which are self-explanatory and are summarised in Table I. The figures for Burdwan, Suri and Maynaguri clays, which are similar in nature to Contai and Kakdwip clays, have been omitted for economy of space.

Table I

[Percentage of added C.T.A B. in terms of b.e.c. for maximum sedimentation volume].

	Original clay.	Oxide-free clay.		
		$<2\mu$ size.	$<0.5\mu$ size.	$1\text{-}2\mu$ size.
Kakdwip	75	40	30	40
Contai	60	40	30	40
Burdwan	50	50	50	50-60
Suri	50	40	...	...
Maynaguri	25	25-30		
Montmorillonite	70			
Illite	50			
Kaolinite	50			
Vermiculite :				
Bagespura	66	66		
Malavangatta	60	60		

FIG. 5

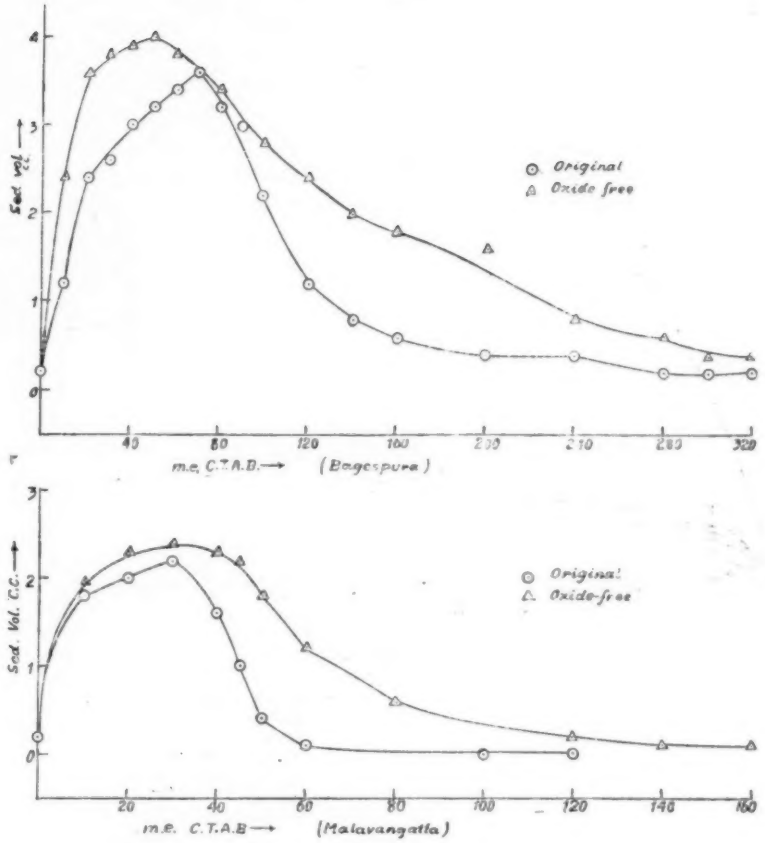


FIG. 6

DISCUSSION

From the amounts of C. T. A. B. (expressed as % b. e. c.) required to impart maximum sedimentation volume to the pure clay minerals and soil clays, shown in the table above, it will be observed that the maximum sedimentation volume occurs, in general, corresponding to the addition of 50-75% of C. T. A. B. Amongst the clay minerals, montmorillonite (aqua-gel) requires the largest amount, followed in order by vermiculite, illite and kaolinite. The soil clays with the free-oxides intact require higher amounts of C. T. A. B. for maximum sedimentation volume, which decreases more markedly in the case of the oxide-free Kakdwip and Contai clays than the rest of the soil clays and the vermiculites.

FIG. 7

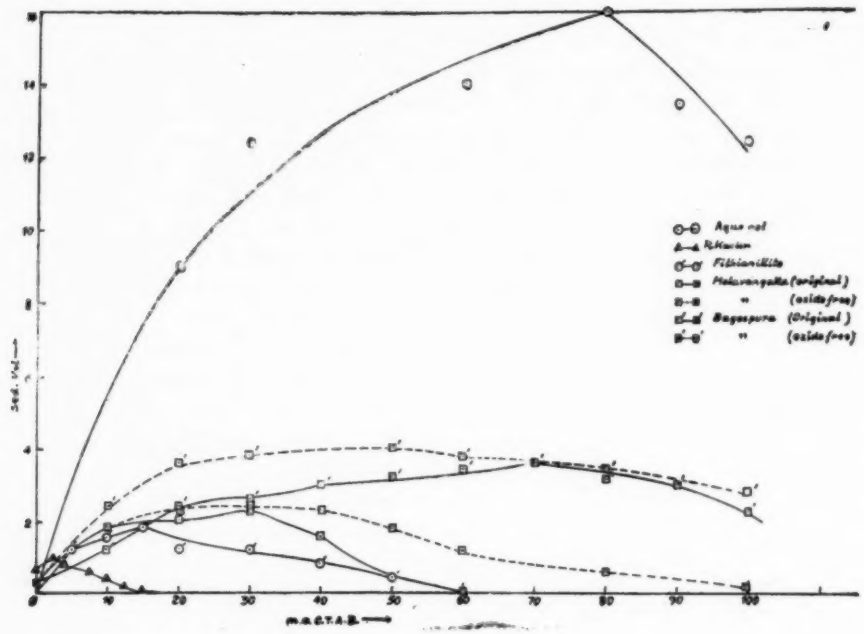
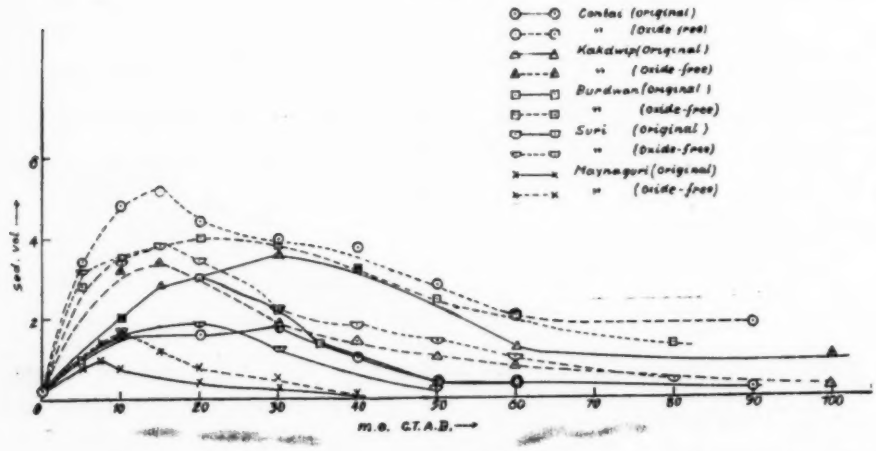


FIG. 8



A comparison of the curves of sedimentation volumes *vs.* concentration of C.T.A.B. for the different clay minerals (Fig. 7) and soil clays (Fig. 8) shows that at any particular concentration of C.T.A.B. (as also of the clay), the sedimentation volumes can be placed in the following sequence: montmorillonite > vermiculite > illite > kaolinite. The sedimentation volumes of soil clays are, in general, much below that of aqua-gel, and

fall in line with vermiculites and illites. The oxide-free soil clays, as already mentioned, have usually somewhat higher sedimentation volumes, the most prominent change being observed in the case of the Contai clay. The Maynaguri clay in the original as well as in the oxide-free conditions shows clearly features similar to kaolinite, the presence of which is also suggested from the X-ray and differential thermal analyses (Adhikari, *loc. cit.*, p. 199).

Sincere appreciation is expressed to Dr. S. K. Mukherjee, Department of Applied Chemistry, for his helpful suggestions and providing laboratory facilities and to the Ministry of Education, Govt. of India, for the grant of a scholarship.

Department of Applied Chemistry,
University College of Science &
Technology, Calcutta-9.

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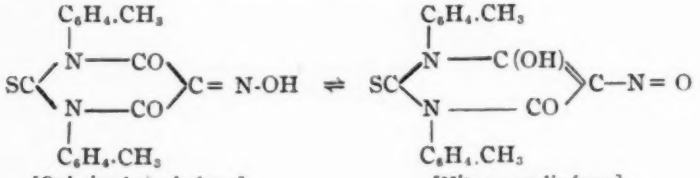
METAL COMPLEXES OF DI-o-TOLYLTHIOVIOLURIC ACID

By R. P. Singh

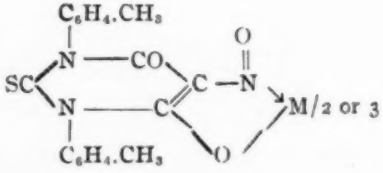
Several metal complexes of di-*o*-tolylthioviolurie acid have been prepared. These highly coloured salts appear to be inner metal complexes of di-*o*-tolylthioviolurie acid.

Complex compounds of various metals with diphenylvioluric acid (*J. Sci. Ind. Res.*, 1956, **15B**, 245) and diphenylthioviolurie acid (*Proc. Ind. Acad. Sci.*, 1946, **23A**, 330) were prepared by the author earlier. The present work deals with similar complexes formed with di-*o*-tolylthioviolurie acid.

Theoretical considerations and the properties of these compounds point out that they are probably inner complexes. The possibility of inner complex salt formation arises wherever acidic and donor functions, such as amino, carbonyl etc., are suitably situated in the same molecule, *i. e.*, in 1 : 4- or 1 : 5-position to one another. The di-*o*-tolylthioviolurie acid molecule, in its nitroso-enolic form, represented below :



contains a replaceable hydrogen atom, which can be replaced by a metal atom during salt formation. The nitrogen atom of the nitroso group can act as a donor and a five-membered ring can thus be formed. Alternatively, if the oxygen atom of the nitroso group acts as a donor, the ring will be six-membered. The salts of di-*o*-tolylthioviolurie acid are perfectly stable at ordinary temperatures, have comparatively low melting points, and are insoluble in water and soluble in organic solvents such as acetone, ethyl alcohol, dioxan etc. These properties as well as the intense colour of these compounds support the view that these salts are inner complexes and can be represented by :



Experimental

Di-o-tolylthioviolurie Acid.—Di-*o*-tolylthiobarbituric acid was prepared by condensing a mixture of di-*o*-tolylthiourea and malonic acid in presence of acetyl chloride.

It was then converted into di-*o*-tolylthiovioluric acid by adding sodium nitrite, followed by the addition of H_2SO_4 (dil.). The crude product, thus obtained, was purified by crystallising from boiling glacial acetic acid, m.p. 200°.

Metallic Salts of Di-o-tolylthiovioluric Acid.—Di-*o*-tolylthiovioluric acid dissolves readily in ammonium hydroxide, affording a blue solution due to the formation of the ammonium salt. The solution was concentrated on a water-bath when the bluish grey crystals of the ammonium salt were diposited. Sodium and potassium salts were similarly obtained by neutralising the acid with the corresponding alkali.

Sal s of other metals were prepared by the addition of a concentrated solution of ammonium salt to a saturated solution of the salt of the metal concerned (vide Table I), when the metal complexes were thrown down as precipitates.

The salts, which were insoluble in water owing to hydrolysis, were dissolved in alcohol or chloroform. Metal and sulphur contents were determined in the complexes by the usual methods (Table I).

TABLE I

Salt.	% Metal in salt.		% Sulphur.		Metal : acid.
	Calc.	Found.	Calc.	Found.	
Na	...	...	8.54	8.58	1 : 1
K	...	...	8.18	8.21	1 : 1
NH_4	...	...	8.65	8.55	1 : 1
Ag	23.47	23.39	6.96	6.94	1 : 1
Fe^{II}	7.36	7.30	8.40	8.45	1 : 2
Fe^{III}	5.04	5.00	8.63	8.60	1 : 3
Al	2.49	2.45	8.86	9.01	1 : 3
Cr	4.69	4.72	8.66	8.66	1 : 3
Cu^{II}	8.28	8.31	8.33	8.42	1 : 2
Ni	7.70	7.76	8.39	8.41	1 : 2
Co	7.73	7.78	8.38	8.50	1 : 2
Mg	3.33	3.31	8.78	8.72	1 : 2
Ca	5.38	5.35	8.60	8.25	1 : 2
Sr	11.06	11.10	8.08	8.00	1 : 2
Ba	16.33	16.21	7.60	7.59	1 : 2
Pb	22.73	22.58	7.02	7.10	1 : 2
Sb	10 34	10.29	8.15	8.01	1 : 3
Bi	16.52	16 49	7.59	7.50	1 : 3
Zn	8.50	8.42	8.32	8.22	1 : 2
Cd	13.76	13 75	7.84	7.95	1 : 2
Hg^{II}	22.17	22.11	7.07	6.99	1 : 2
Mn	7.23	7.10	8.43	8.40	1 : 2
Au	15.74	15.77	7.66	7.51	1 : 3
Ce^{III}	9.05	9.10	...	...	1 : 4
Pt^{VI}	12.17	12.18	7.98	7.85	1 : 4
UO_2^{2+}	24.44	24.51	6.57	6.59	1 : 2
Th	14.15	14.12	7.80	7.81	1 : 4

All the salts of di-*o*-tolylthiovioluric acid are crystalline and stable at ordinary temperatures. The silver salt, obtained as a green precipitate, is, however, unstable and

decomposes on exposure to sunlight. The complexes were dissolved in aqueous acetone and various tests for the respective cations were performed. The solution responded to most of the tests for the respective cations, showing that there was some dissociation in most cases. The following exceptions were noted :

(1) In the case of the copper complex, a dark pinkish precipitate was obtained with potassium ferrocyanide in place of the reddish brown copper ferrocyanide.

(2) The calcium complex gave a light greenish precipitate with potassium chromate solution.

(3) The platinum complex gave a yellow precipitate on passing H_2S through the solution.

The properties of the salts are recorded in Table II. Values of absorption maxima were determined by using a Hilger constant-deviation spectrograph.

TABLE II

Salt.	Colour in Solid state.	Colour in Acetone.	Decomp. temp	$\lambda_{max.}$
Ag	Green	Green	...	...
Pb	Greyish brown	Brown	221°	...
Hg^{II}	Buff	Buff	182°	4610 A
Bi	Orange-brown	Greenish yellow	177°	4951
Cu^{II}	Brown	Light brown	255°	4984
Cd	,,	Light brown	215°	4368
Sb	Light reddish	Yellowish	205°	6742
Sn	Red	Light red	181°	4542
Fe^{II}	Deep blue	Deep blue	187°	5662
Fe^{III}	Dark green	Green	179°	5549
Al	Reddish brown	Reddish brown	203°	4248
Cr	Brown	Light brown	200°	4478
Co	Dark brown	Dark brown	210°	5763
Ni	Yellowish brown	Yellowish brown	235°	5588
Mn	Grey	Bluish grey	243°	4567
Zn	Light brown	Brown	212°	4736
Ca	Light pink	Pinkish yellow	>270°	5356
Ba	Dark pink	Pink	,,	5890
Sr	Violet-pink	Pinkish orange	,,	5787
Mg	Light brown	Light brown	,,	4247
Ce^{III}	Brown	Brown	230°	...
Th	Light brown	Brown	202°	4327
Au	Dark brown	Brown	217°	5254
Pt	Light brown	Brown	197°	4834
U	Reddish brown	Brown	207°	4112
NH_4	Bluish grey	Greenish blue	185°	6957
K	Brown	Light brown	182°	4175
Na	Dark green	Emerald green	...	...

CHEMISTRY DEPARTMENT,
UNIVERSITY OF DELHI,
DELHI-8.

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DICYANO COBALT (III) BIGUANIDE COMPLEXES

By Nihar Ranjan Sengupta and Priyadaranjan Rây

By the action of potassium cyanide on a solution of cobaltic *tris*-biguanide (or substituted biguanide) chloride at the temperature of water-bath, a univalent cationic dicyanocobaltic *bis*-biguanide (or substituted biguanide) base has been prepared in the form of golden yellow crystals, sparingly soluble in water. Starting from the complex base, several salts (chloride, sulphate, nitrate, thiocyanate, etc.) have been obtained. These may be represented by the general formula :

$$[Co(RR'—BigH)_2\ (CN)_2]X,$$

where R = H, CH_3, C_2H_5. $CH_3.(CH_2)_5$, C_6H_5 or $C_6H_5CH_2$; R' = H, CH_3, C_2H_5 and X = OH or any univalent anion or an equivalent of polyvalent anion. Here RR'-BigH represents a molecule of biguanide. Their conductivity values in solution agree with the composition as uni-univalent electrolyte.

Similar reactions of potassium cyanide with dicobaltic *tris*-dibiguanides, such as ethylene-, hexamethylene- and *m* phenylene-dibiguanide gave rise to the corresponding dicyano bases, from which by the action of ammonium salts the corresponding salts were prepared. The composition of these can be represented by the general formula :

$$[Co.R''(BigH)_2\ (CN)_2]X,$$

where R''$(BigH)_2$ = a molecule of ethylene-, hexamethylene- or *m*-phenylene-dibiguanide, and X = OH, Cl or $\frac{1}{2}SO_4$.

All these dicyanocobaltic complexes have been found to be diamagnetic and, hence, they belong to the type of inner-level octahedral complexes with d^2sp^3 hybrid covalent bonds, presumably with *trans* configuration.

The formation of a substituted cyanocobaltiate, the nitropentacyanocobaltiate, in solution was first established by Jackson and Comey (*Ber.*, 1896, **29**, 1020 ; *J. Amer. Chem. Soc.*, 1897, **19**, 271). Manchot and Gall (*Ber.*, 1926, **59**, 1959), however, succeeded in preparing the pentacyanocarbonyl cobaltiate in a crystalline state and studied its properties. But the main contribution to the subject of substituted cyanocobaltiates may be attributed to Rây and coworkers (Rây, this *Journal*, 1927, **4**, 325 ; *Z. anorg. Chem.*, 1932, **208**, 392 ; Rây and Dutt, *ibid.*, 1937, **234**, 65 ; Rây and Gupta Chowdhury, *ibid.*, 1934, **220**, 154), who described the preparation and properties of a large number of substituted penta- and tetra-cyanocobaltic complexes. These are : (*a*) thiosulphato-pentacyanocobaltiate (*b*) μ-sulphito-decacyanodicobaltiate, (*c*) aquo-pentacyanocobaltiate and (*d*) disulphito-tetracyanocobaltiate. In addition to a number of metallic salts, the corresponding free complex acids were also isolated. The constitution of the μ-sulphito-decacyanodicobaltiate was also discussed.

In all these compounds the complex entity containing the metal atom forms an anion. The first instance of a cationic cyanocobaltic complex is furnished by the monocyano-aquo-tetrammine cobaltic chloride, described by Hoffmann and Reinsch (*Z. anorg. Chem.*, 1898, **16**, 399). A series of salts of a univalent cationic dicyano-*bis*-ethylenediamine cobaltic complex has been described by Rây and Sarma (this *Journal*, 1951, **28**, 59). The thiosulphate salt of this complex cation was

prepared by the action of potassium cyanide on a solution of dithiosulphato-*bis*-ethylenediamine cobaltiate.

In continuation of the previous work of Rây *et al.*, it was considered worthwhile to investigate the action of potassium cyanide on cobaltic *tris*-biguanide compounds. This has led to the preparation of a number of substituted cyanocobaltic biguanide complexes, described in the present paper.

When cobaltic *tris*-biguanide chloride is allowed to react with potassium cyanide in aqueous solution on the water-bath, the pinkish red colour of the solution changes to orange-yellow and from this, golden yellow shining crystals of the dicyanocobaltic *bis*-biguanide in the form of an anhydro base separate. The reaction may be represented as:

$$[Co'RR'-BigH)_3]Cl_3 + 2KCN + H_2O$$
$$= [Co'(RR'-BigH)_2(CN)_2]OH + 2KCl + (RR'—BigH)HCl$$

$-H_2O$ ↙ (in solution) ↘ $(NH_4)X$

$[RR'\text{-BigH-Co}(RR'—Big).(CN)_2]$ (Golden yellow crystals) → $[Co(RR'—BigH)_2(CN)_2]X$

where RR'-BigH = a molecule of biguanide, $C_2N_5H_7$, or a mono- or di-substituted biguanide, $C_2N_5H_6R$ or $C_2N_5H_5RR'$ and X = any univalent anion or an equivalent of a polyvalent anion.

The hydrated base may be formed in aqueous solution, from which by the action of ammonium salts the corresponding complex cobaltic salts, such as sulphate, chloride, thiocyanate, etc., can be prepared. The complex chloride is fairly soluble in water, and from its solution by adding alkali salts, the corresponding sparingly soluble salts can also be prepared. The same reaction of potassium cyanide on the cobalt *tris*-substituted biguanides, such as, methyl-, ethyl-, dimethyl-, diethyl-, hexyl-, phenyl and benzyl-biguanide, gives rise to the corresponding dicyanocobaltic substituted biguanide bases, and from the latter by the action of ammonium salts, the corresponding salts can be prepared. The solubility of the dicyanocobaltic biguanide complexes in water decreases with the increase in the molecular weight of the substituent in the biguanide molecule.

The complex dicyanocobaltic *bis*-dimethylbiguanide sulphate (yellow) on heating to 100° for two hours changes to green. On cooling below 100°, the reverse change occurs without any alteration in its composition. This seems to suggest a *cis-trans* isomeric transformation under the influence of heat.

Dicobaltic *tris*-dibiguanides, such as ethylene-, hexamethylene- and *m*-phenylene-dibiguanide, similarly react with potassium cyanide solution to yield dicyanocobaltic dibiguanide bases. The bases of dicyanocobaltic ethylene- and hexamethylene-dibiguanide, being extremely soluble in water, could not, however, be isolated in the solid state. The corresponding complex salts, on the other hand, were obtained by the action of ammonium salts on the complex base in solution.

$$[R''(BigH)_2.Co.R''(BigH)_2.Co.R''(BigH)_2]X_6 + 4KCN + 2H_2O =$$
$$2[R''(BigH)_2.Co.(CN)_2]OH + 4KX + R''(BigH)_2.2HX$$

where R″(BigH)$_2$=one molecule of ethylene-, hexamethylene- and *m*-phenylene-dibiguanide.

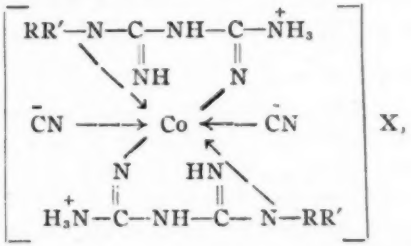
The conductivity measurement of their complex chlorides demonstrates that these can be represented as uni-univalent electrolytes, which suffer slow hydrolysis in aqueous solution at 35°.

All these cyanocobaltic biguanide compounds are diamagenetic, as is to be expected, and, hence, belong to the type of the inner-metallic penetration complexes with octahedral d^2sp^3 hybrid bonds.

The only possible constitution for a compound of the composition,

$$[Co(RR'-BigH)_2\ (CN)_2]X,$$

is given by the following configuration :



(where R=H, CH_3, C_2H_5, $CH_3(CH_2)_5$, C_6H_5 or $C_6H_5.CH_2$; R′=H, CH_3 or C_2H_5, and X=OH or any univalent anion) with the two cyanogen groups occupying *trans* positions.

For a dibiguanide complex, four of the co ordination positions of the metal atom are occupied by one and the same dibiguanide molecule, $[(CN)_2.Co.R''(BigH)_2]X$, where R″(BigH)$_2$=ethylene-, hexamethylene- and *m*-phenylene-dibiguanide, and X=OH, Cl or $\frac{1}{2}SO_4$.

Such an arrangement of hexamethylene-dibiguanide around a single metal atom under normal condition is extremely unlikely. In all such cases, the complex ion possibly consists at least of dimeric aggregates. This is supported by the fact that all these dicyanodibiguanide complexes readily form gummy masses on keeping or drying (vide Experimental).

EXPERIMENTAL

Dicyanocobaltic bis-*Biguanide* (*anhydrobase*).—Cobaltic *tris*-biguanide chloride was prepared according to the method of Rây and Dutt (this *Journal*, 1939, **16**, 621). A solution of potassium cyanide (1.75 g. in 20 c.c. of water) was added to that of the cobaltic *tris*-biguanide chloride (4.70 g. in 50 c.c. of warm water). The mixture was filtered and the filtrate heated on a water-bath for about ten minutes with constant stirring, when some shining golden yellow crystals separated out. These were collected on the filter-bed, washed thoroughly first with cold water, then with absolute alcohol and finally dried over KOH and $CaCl_2$. { Found : Co, 18.96; N, 54.09 ; CN, 16.36. $[Co(H_2\text{-}BigH)(H_2\text{-}Big)(CN)_2]$ requires Co, 18.88 ; N (total), 53.91 ; CN, 16.67% }.

The complex anhydrobase is sparingly soluble in cold water, moderately in hot water, but insoluble in alcohol. In solution it obviously forms the hydrated base, $[Co(H_2\text{-}BigH)_2(CN)_2]OH$. The aqueous suspension of the complex base reacts alkaline to litmus, liberates ammonia from ammonium salts with the formation of the corresponding salts of the complex base. It absorbs CO_2 from moist air. Acids decompose it readily to give a pink solution. The complex base is easily decomposed by warming with mercuric oxide.

Dicyanocobaltic bis-*biguanide sulphate* was prepared by digesting the complex base with a strong solution of ammonium sulphate at room temperature for about 4 hours. The golden yellow complex base changed to a bright yellow product. This was filtered, washed thoroughly with water and dried in air. { Found : Co, 15.56 ; SO_4, 12.83 ; N, 44.22 ; H_2O (by loss at 110°), 4.96. $[Co(H_2\text{-}BigH)_2(CN)_2]_2.SO_4.H_2O$ requires Co, 15.54 ; SO_4, 12.67 ; N (total), 44.33 ; H_2O, 4.75% }.

Chloride.—The complex base was treated with a strong solution of ammonium chloride on the water-bath for about an hour when a clear solution was obtained, which was filtered hot. The filtrate was allowed to cool slowly when some shining orange-yellow crystals separated from the solution. These were filtered, washed first with ice-cold water, then with absolute alcohol and finally dried in air. { Found : Co, 16.87 ; Cl, 10.46 ; N, 48.04. $[Co(H_2\text{-}BigH)_2(CN)_2]Cl$ requires Co, 16.90 ; Cl, 10.19 ; N(total), 48.21% }.

Thiocyanate.—The yellow complex thiocyanate was prepared from the complex base by digestion with a strong solution of ammonium thiocyanate. This was filtered, washed and dried as in the previous cases. { Found : Co, 15.80 ; SCN, 15.95 ; N, 49.01. $[Co(H_2\text{-}BigH)_2(CN)_2]SCN$ requires Co, 15.88 ; SCN, 15.64 ; N (total), 49.08% }.

The *nitrate* was prepared by the double decomposition of the complex chloride and alkali nitrate in solution. The yellow complex nitrate was filtered, washed with water and dried in air. { Found : Co, 15.62 ; NO_3, 16.49. $[Co(H_2\text{-}BigH)_2(CN)_2](NO_3)$ requires Co, 15.70 ; NO_3, 16.54% }.

In a similar manner the following dicyanocobaltic compounds of substituted biguanides were prepared and studied.

Dicyanocobaltic bis-*Methylbiguanide Complexes*

1. *Base* : { Found : Co, 15.81 ; N, 44.85 ; CN, 13.42 ; H_2O (by loss at 110°), 9.43. $[Co(CH_3.H\text{-}BigH)_2(CN)_2]OH.H_2O$ requires Co, 15.67 ; N (total), 44.69 ; CN, 13.83 ; H_2O (total), 9.55% }.

2. *Sulphate* : { Found : Co, 14.23 ; SO_4, 11.71 ; N, 40.54 ; H_2O (by loss at 110°), 6.57. $[Co(CH_3.H\text{-}BigH)_2(CN)_2]_2\,SO_4.2.5\,H_2O$ requires Co, 14.17 ; SO_4, 11.54 ; N (total), 40.39 ; H_2O, 6.49% }.

3. *Chloride* : { Found : Co, 14.53 ; Cl, 9.05 ; N, 41.89 ; H_2O (by loss at 110°), 6.92. $[Co(CH_3.H\text{-}BigH)_2(CN)_2]Cl.\,1.5\,H_2O$ requires Co, 14.62 ; Cl, 8.80 ; N (total), 41.64 ; H_2O, 6.69% }.

Dicyanocobaltic bis-*Dimethylbiguanide Complexes*

Base: { Found : Co, 15.32 ; N, 43.56 ; H_2O (by loss at 110°), 4.74. $[Co(Me_2\text{-}BigH)_2(CN)_2]OH$ requires Co, 15.26 N (total), 43.43 ; H_2O, 4.67% }.

2. *Sulphate*: { Found : Co, 14.03 ; SO_4, 11.79 ; N, 40.54. $[Co(Me_2.BigH)_2\text{-}(CN)_2]_2\ SO_4$ requires Co, 14.13 ; SO_4, 11.52 ; N (total), 40.30% }.

Dicyanocobaltic bis-*Ethylbiguanide Complexes*

Base: { Found : Co, 15.19 ; N, 43.49 ; H_2O (by loss at 110°), 4.84. $[Co(Et.\text{-}H\text{-}BigH)_2(CN)_2](OH)$ requires Co, 15.26 ; N (total), 43.43 ; H_2O, 4.67% }.

2. *Sulphate*: { Found: Co, 13.51 ; SO_4, 11.15 ; N, 38.70 ; H_2O (by loss at 110°), 4.38. $[Co(Et.H\text{-}BigH)_2(CN)_2]_2\ SO_4.2H_2O$ requires Co, 13.54 ; SO_4, 11.04 ; N (total), 38.63 ; H_2O, 4.14% }.

Dicyanocobaltic bis-*Diethylbiguanide Complexes*

1. *Base* (anhydro): { Found: Co, 13.85 ; N, 39.36. $[Co(Et_2.Big)(Et_2.BigH)\text{-}(CN)_2]$ requires Co, 13.90 ; N (total), 39.54% }.

2. *Sulphate*: { Found: Co, 12.40 ; SO_4, 10.17 ; H_2O (by loss at 110°), 1.96. $[Co(Et_2.\ BigH)_2(CN)_2]_2\ SO_4.H_2O$ requires Co, 12.23 ; SO_4, 9.96 ; H_2O, 1.87% }.

Dicyanocobaltic bis-*Hexylbiguanide Complexes*

1. *Base*: { Found: Co, 11.41 ; N, 32.25 ; H_2O (by loss at 110°), 6.78. $[Co\text{-}(C_6H_{13}.H\text{-}BigH)_2(CN)_2]OH.H_2O$ requires Co, 11.45 ; N (total), 32.60 ; H_2O (total), 6.99% }.

2. *Sulphate* : { Found: Co, 10.58 ; SO_4, 8.76 ; H_2O (by loss at 110°), 3.58. $[Co(C_6H_{13}.H\text{-}BigH)_2(CN)_2]_2\ SO_4.2.5H_2O$ requires Co, 10.69 ; SO_4, 8.70 ; H_2O, 4.10% }.

Dicyanocobaltic bis-*Phenylbiguanide Complexes*

Base : { Found : Co, 11.27 ; CN, 9.39 ; N, 31.92 ; H_2O (by loss at 110°), 11.82. $[Co(C_6H_5.H\text{-}BigH)_2(CN)_2]OH.2.5\ H_2O$ requires Co, 11.20 ; CN, 9.86 ; N (total), 31.87 ; H_2O (total), 11.95% }.

2. *Chloride*: { Found : Co, 11.70 ; Cl, 7.38 ; N, 33.82. $[Co(C_6H_5.H\text{-}BigH)_2(CN)_2]Cl$ requires Co, 11.77 ; Cl, 7.09 ; N (total), 33.57% }.

Dicyanocobaltic bis-*Benzylbiguanide Complexes*

1. *Base*: { Found : Co, 11.49 ; N, 32.76 ; H_2O (by loss at 110°), 3.74. $[CoC_6H_5.\text{-}CH_2.H\text{-}BigH)_2(CN)_2](OH)$ requires Co, 11.55 ; N (total), 32.94 ; H_2O, 3.53% }.

2. *Sulphate*: { Found : Co, 10.28 ; SO_4, 7.97 ; N, 28.78 ; H_2O (by loss at 110°), 7.85. $[Co(C_6H_5.CH_2.H\text{-}BigH)_2(CN)_2]_2\ SO_4.\ 5H_2O$ requires Co, 10.05 ; SO_4, 8.19 ; N (total), 28.69 ; H_2O, 7.67% }.

3. *Chloride*: { Found : Co, 10.15 ; Cl, 6.34 ; N, 29.46 ; H_2O (by loss at 110°), 7·68. $[Co(C_6H_5.CH_2.H\text{-}BigH)_2(CN)_2]Cl.\ 2.5\ H_2O$ requires Co, 10.35 ; Cl, 6.19 ; N (total), 29.29 : H_2O, 7.83% }.

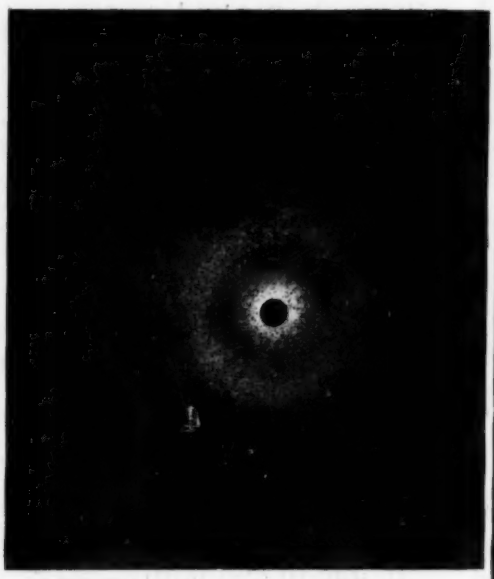
Dicyanocobaltic Ethylenedibiguanide Chloride

Dicobaltic *tris*-ethylenedibiguanide chloride was prepared according to the method described by Ray and Rây (unpublished work). A solution of KCN (0.4 g. in 10 c.c. of water) was added to a suspension of the former (2 g. in 20 c.c. of water) and the mixture was heated on the water-bath till a clear yellow solution was obtained. This was filtered hot and the filtrate after cooling was treated with a few c.c. of a strong solution of ammonium chloride in the cold, when a yellow precipitate of the complex chloride separated out. This was washed several times with water by decantation. The product was finally filtered, washed twice or thrice with water, and dried over $CaCl_2$.

It formed, when dried, an orange-yellow gummy mass, almost insoluble in water. The precipitate, first obtained by the addition of ammonium chloride, was more or less crystalline, but on filtration it gradually changed into a sticky mass. Both the dry and freshly precipitated moist products were examined by the X-ray diffraction method. The results, as shown in Figs. 1 and 2, indicate rather weakly crystalline character of the freshly prepared moist substance and the amorphous nature of the dry specimen.

FIG. 1

FIG. 2



The phenomenon is suggestive of polymerisation. { Found : Co, 13.73 ; Cl, 8.08 ; N, 39.03 ; H_2O (by loss at 110°), 12.30. $[C_2H_4(BigH)_2.Co.(CN)_2]Cl.3H_2O$ requires Co, 13.77 ; Cl, 8.29 ; N (total), 39.21 ; H_2O, 12.60% }.

Dicyanocobaltic hexamethyenedibiguanide chloride was prepared like the previous compound. { Found : Co, 12.62 ; Cl, 7.22 ; N, 35.34 ; H_2O (by loss at 110°),

9.38. $[C_6H_{12}(BigH)_2.Co.(CN)_2]Cl.2.5H_2O$ requries Co, 12.41 ; Cl, 7.46 ; N (total), 35.33 ; H_2O. 9.46% }.

Dicyanocobaltic m-*Phenylenedibiguanide Complexes*

1. *Base.*—Dicobaltic *tris-m*-phenylenedibiguanide chloride was prepared according to the method described by Rây and Das Sarma (this *Journal*, 1949, **26**, 137). The chloride of the complex (1 g. in 50 c.c. of water) was treated with KCN solution (0.25 g. in 10 c.c. of water) and the mixture was heated on the water-bath till the red colour of the solution changed to orange-yellow. The mixture was filtered and the filtrate on cooling deposited orange-yellow crystals of the complex base. These were filtered, washed with ice-cold water, and dried over KOH and $CaCl_2$. { Found : Co, 12.89 ; CN, 11.09 ; N, 37.72 ; H_2O (by loss at 110°), 13.82. $[C_6H_4(BigH)_2.Co(CN)_2]$-(OH). $2.5H_2O$ requires Co, 13.14 ; CN, 11.58 ; N (total), 37.42 ; H_2O (total), 13.81% }.

2. The *sulphate* was prepared as usual by digesting the moist complex base with ammonium sulphate. { Found : Co, 11.37 ; SO_4, 9.19 ; N, 32.30; H_2O (by loss at 110°), 15.75. $[C_6H_4(BigH)_2.Co.(CN)_2]_2\,SO_4.9H_2O$ requires Co, 11.41 ; SO_4, 9.30 ; N (total), 32.56 ; H_2O, 15.70% }.

TABLE I

Conductivity measurements.

Temp. = 35° ± 0.1°.

1. Dicyanocobaltic *bis*-biguanide chloride.

'v' (litres)	N/32.	N/64.	N/128.	N/256.	N/512.	N/1024.
Λ_v	90.82	95.43	105.6	110.4	120.9	125.4
Λ_∞	102.0	103.7	112.1	115.2	124.7	128.0

2. Dicyanocobaltic *bis*-methylbiguanide chloride.

	N/128.	N/256.	N/512.	N/1024.
Λ_v	95.41	108.1	119.9	127.3
Λ_∞	101.3	112.8	123.7	129.9

3. Dicyanocobaltic *bis*-benzylbiguanide chloride.

	N/256.	N/512.	N/1024.	N/2048.
Λ_v	105.4	115.4	124.6	125.4
Λ_∞	110.0	119.1	127.2	127.3

$\Lambda_\infty = \Lambda_v\,(1 + 0.692 \times n_1.n_2 \times v^{-\frac{1}{2}})$ (Walden's form 1a) [where n_1 and n_2 are the valencies of the cations and anions respectively and 'v' indicates dilution in litre].

The results are in good agreement for a uni-univalent electrolyte. The variation of Λ_∞ calculated from Λ_v indicates that the complex undergoes hydrolysis in dilute solutions at 35° ± 0.1°.

Magnetic Susceptibilities

The susceptibilities were measured in a Guoy's balance with a field strength of 8.98×10^3 gauss.

TABLE II

	Substance.	$\chi_g \times 10^6$.	$\chi_M \times 10^6$
1.	*D.C. *bis*-B (Golden yellow)	−0.5224	−161.9
2.	D.C. *bis*-B sulphate (Bright yellow)	−0.1821	−67.20
3.	D C. *bis*-methyl-B (Yellow)	−0.5055	−190.0
4.	D.C. *bis*-benzyl-B (Golden yellow)	−0.2391	−121.9
5.	D.C. *m*-phenylene-B (Orange-yellow)	−0.4635	−208.:

* D.C denotes dicyanocobaltic and B, biguanide.

Method of Analysis

Cobalt in these complex cyano-biguanide compounds was estimated as $CoSO_4$ after ignition with strong H_2SO_4. Total nitrogen was estimated as usual by Kjeldahl's method. For the estimation of cyanogen, the substance was digested with HgO in a boiling solution. From the filtrate containing mercuric cyanide, mercury was removed as HgS by ammoniacal H_2S in presence of zinc sulphate. From the filtrate cyanogen was then precipitated as AgCN by the addition of silver nitrate solution containing a little nitric acid (Treadwell and Hail, "Analytical Chemistry", Vol. II). Chlorine, when present as in the complex chloride, was estimated as AgCl, after removing the cyanogen by boiling with dilute acetic acid (Williams, "Cyanogen Compounds").

DEPARTMMENT OF INORGANIC CHEMISTRY,
INDIAN ASSOCIATION FOR THE
CULTIVATION OF SCIENCE,
JADAVPUR, CALCUTTA-32.

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ORGANIC SULPHUR COMPOUNDS. PART III. REACTIONS OF BENZALDEHYDE WITH SODIUM DISULPHIDE: ISOLATION OF A NEW PRODUCT

By K. A. Latif*, M. A. Razzaq, S. K. Adhikari and M. M. Eunus

On repeating Bruni's experiment to obtain dithiobenzoic acid, a new sulphur-containing compound (m.p 153°), has been obtained, by using benzaldehyde and sodium disulphide (Na_2S, $9H_2O$ and sulphur in equimolar proportion) in the proportion of 3:1 in aqueous-alcoholic medium.

Bruni reported (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 533) that dithiobenzoic acid could be obtained by the action of ammonium polysulphide on benzaldehyde according to the course of the reaction:

$$C_6H_5CHO + (NH_4)_2S_2 \longrightarrow C_6H_5C(=S)SNH_4 + NH_4OH$$

$$C_6H_5C(=S)SNH_4 + H^+ \longrightarrow C_6H_5.C(=S)SH + NH_4^+$$

The results, obtained by other alkali polysulphides were unsatisfactory.

From our interest to obtain dithiobenzoic acid for some other purpose, we repeated the experiment of Bruni, using sodium polysulphide (to be exact, a solution of $Na_2S.9H_2O$ to which one equivalent of sulphur was added) and the result obtained was quite interesting. The main product turned out to be an apparently new sulphur-containing product that came out in fine crystalline form from acetone, melting at 153°. It is quite soluble in benzene, ether, chloroform, carbon disulphide etc., while moderately soluble in acetone, and only sparingly so in alcohol and glacial acetic acid. The formation of this compound was found to be dependent on certain optimum conditions and, in particular, the presence of alcohol and water in more or less fixed proportions. For example, all other conditions remaining the same, the product is not apparently formed either in aqueous or pure alcoholic medium; the highest yield has been recorded when alcohol and water are present in approximately 1:1 proportion. Moreover, for the maximum yield, the required proportion of sodium disulphide and benzaldehyde appears to be 3:1.

From the mother-liquor, benzoic acid and benzyl alcohol were isolated. No appreciable portion of dithiobenzoic acid could, however, be isolated. Though the mother-liquor gave tests for the presence of a thio acid, it could not be isolated owing probably to its decomposition into benzoic acid.

The purity of this crystalline product as a single substance has been established by subjecting it to chromatographic studies (both column and paper). Structural studies of this crystalline product appear in Part IV of this series.

* Present address: Department of Chemistry, Rajshahi University, East Pakistan.

Attempts to prepare similar products from other aromatic aldehydes did not succeed. Only in the case of vanillin, a thio acid could be detected and ultimately converted into the corresponding disulphide.

EXPERIMENTAL

Reaction of Benzaldehyde with Sodium Disulphide Solution.—Crystalline sodium sulphide, Na_2S, $9H_2O$ (24 g., 0.1 *M*) was dissolved in water (40 c.c.). Sulphur (3.2 g., 0.1 *M*) was added to this solution and stirred continually till a fairly clear solution was obtained. It was filtered.

This solution (of Na_2S_2) was transferred to a flask containing alcohol (40 c.c.) and benzaldehyde (3.6 g., 0.033 *M*). The resulting mixture was refluxed for 2 hours (water-bath) and allowed to stand overnight when crystals appeared. These were separated by filtration and recrystallised from acetone, m.p. 153°. Both the crystals and the filtrate were kept for further study.

Treatment of the Filtrate.—The filtrate was diluted with a large excess (about four times its volume) of water, extracted with ether and the two layers were separated. The ether extract was dried over $CaCl_2$ and distilled. After removal of the organic solvents, the distillation was carried out under reduced pressure (15 mm) using an efficient fractionating column. Two main fractions were collected: (*a*) benzaldehyde (0.6 g.) at 102-104°, confirmed by forming a semicarbazone, m.p. 222° (mixed m.p. with an authentic sample of benzaldehyde semicarbazone showing no depression) and (*b*) benzyl alcohol (0.34 g.) at 110-112°; n_D^{32} 1.5290; forms a 3:5-dinitrobenzoate, m.p. 112° (mixed m.p. with an authentic sample of benzyl 3:5-dinitrobenzoate showing no depression). None of these fractions or their derivatives gave any test for sulphur. An aliquot portion of the original sample (as obtained after evaporation of ether) was tested for the presence of benzylmercaptan by the action of 2:4-dinitrobromobenzene (Bost *et al.*, *J. Amer. Chem. Soc.*, 1932, **54**, 1985), but no derivative was formed.

An aliquot portion of the aqueous extract was treated with lead acetate solution, when a beautiful brown precipitate appeared which decomposed very quickly into a black precipitate. This is indicative of the presence of a thio acid (Gilman, "Advanced Organic Chemistry", Vol. I, p. 930). The entrire solution was then acidified with H_2SO_4 (dil.), when a heavy precipitate appeared. The residue after filtration was treated with dilute $NaHCO_3$ solution and filtered. The residue was sulphur (m.p. 118°, confirmed by mixed m.p. determination and from the smell of SO_2 on burning). The filtrate on acidification yielded benzoic acid (1.1 g.), m.p. 121° (mixed m.p.).

Chromatographic Treatment of the Crystals

(*a*) *Column chromatography.*—A column of alumina was prepared by pouring a suspension of pure alumina (for chromatography) in benzene through a glass tube (length 18", diameter 1¼") having a stop-cock and a packing of glass wool at the bottom, the column being never allowed to get dry.

About 2 c.c. of a fairly concentrated solution of the substance (purified by repeated crystallisation from acetone) in benzene was made and allowed to pass through the column, when a coloured band was formed at the top. Fresh solvent was allowed to pass through the column, when the adsorption band started to move but did not spread out into distinct layers. Ultimately it passed out of the column and was collected in a receiver. On evaporation, crystals were obtained which had the same physical properties as that of the original substance. This was further subjected to paper chromatographic analysis.

(*b*) *Paper chromatography.*—A 2% solution of the original substance in benzene was put near one end of a sheet of filter paper as a tiny drop and it was allowed to dry off. Another 2% solution of the product obtained by column chromatography was placed on the same end of the paper as a small drop (about 3″ apart) and was also allowed to dry off. This sheet of paper was then suspended freely in a closed vessel.

n-Butyl alcohol (40 c.c.), acetic acid (10 c.c.) and water (50 c.c.) were shaken together and allowed to stand. The aqueous layer that separated was taken and placed at the bottom of that glass vessel and then the whole thing was allowed to stand overnight.

The alcoholic layer from the above was placed in a boat at the top of the vessel and the tip of the filter paper was allowed to touch this liquid. The solvent passed slowly downward past the two drops. After 12 hours, the paper was taken out from the chamber and allowed to dry off. The paper was then sprayed with a solution of benzidine-trichloroacetic acid complex and two continuous parallel bands from the two spots were found to appear. These two bands were similar in size, shape and colour. No separate bands from either of the spots were formed.

Reaction of Vanillin with Sodium Disulphide.—To a solution of Na_2S, $9H_2O$ (2.4 g.) in about 15 c.c. of water sulphur (0.32 g.) was added and the mixture was stirred till a clear solution was obtained. It was filtered and to this filtrate alcohol (15 c.c.) and vanillin (1.5 g.) were added. The mixture was refluxed for 1 hour and then cooled overnight. When alcohol was evaporated off slowly, fine, white, needle-shaped crystals appeared (1.8 g.), m.p. 203° (decomp.). This compound was highly soluble in water and when this aqueous solution was treated with I_2 in KI solution, a precipitate appeared. This precipitate was crystallised from rectified spirit, m.p. 173°. [Found: S, 17.47. Calc. for *bis*-(3-methoxy-4-hydroxybenzoyl) disulphide, $C_{16}H_{14}O_6S_2$: S, 17.48%].

CHEMISTRY DEPARTMENT,
DACCA UNIVERSITY, RAMNA,
DACCA, E. PAKISTAN.

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ORGANIC SULPHUR COMPOUNDS. PART IV. REACTION OF BENZALDEHYDE WITH SODIUM DISULPHIDE : CONSTITUTION OF THE NEW PRODUCT

By K. A. Latif,* S. K. Adhikari and M. M. Eunus

The approximate constitution of the new sulphur-containing product, obtained by the reaction of benzaldehyde and sodium disulphide, has been worked out.

The isolation of an apparently new product by the reaction of benzaldehyde and sodium disulphide has already been reported (this *issue*, p. 209). On repeated crystallisation from acetone, the compound melts sharply at 153° and is neutral in character, having no reaction either with an acid or a base (hot or cold). From the percentage composition and the molecular weight, the molecular formula of the compound has been established as $C_{25}H_{21}OS$. The oxygen atom in the compound is present as a ketonic group, as is evident from the formation of a semicarbazone (m.p. 215°), a 2 : 4-dinitrophenylhydrazone (m.p. 210°), a phenylhydrazone (m.p. 120°), an oxime (m.p. 63°) and from lack of any reaction with dimedone. The infra-red spectrum (Fig. 1) also shows an absorption band (at 6.0μ), characteristic of a carbonyl group, though the position is slightly shifted towards the right, probably indicating that the carbonyl group is adjacent to a phenyl group (Cromwell *et al.*, *J. Amer. Chem. Soc.*, 1949, 71, 3337). This carbonyl group has been found to be quite resistant to reduction by aluminium *iso*propoxide (Meerwein-Pondorf-Verley method), but by reduction with zinc-mercury amalgam and concentrated hydrochloric acid (Clemmensen method), an amorphous solid (m.p. 69°) has been obtained which shows no reaction for a carbonyl group, though still responds to test for sulphur.

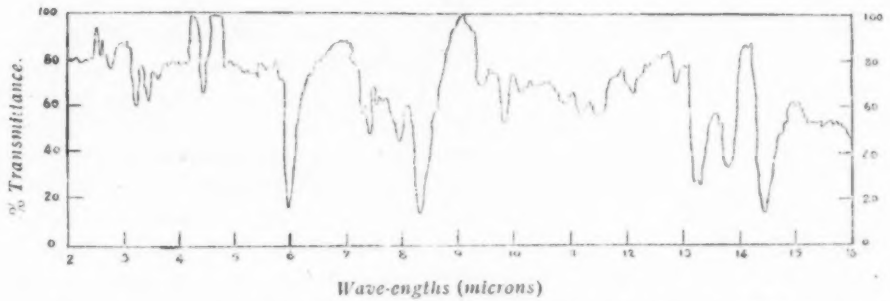
The compound remains unchanged on subjecting to hypohalite oxidation, but on refluxing with $KMnO_4$ in acetone medium, three moles of benzoic acid are obtained for every mole of the compound used. This shows that it contains three phenyl groups in the molecule, each group having a side chain attached to it.

Regarding the nature of the sulphur atom, though the preparation of a sulphone derivative has not yet been successful, the presence of the characteristic band at 14.4 μ is a strong indication of its presence as a C—S—C linkage. That the sulphur atom is not present as a thione linkage (>C=S) has been proved by the absence of any reaction with oxalyl chloride or 10% alcoholic alkali (Schönberg and Asker, *J. Chem. Soc.*, 1946, 608). The lack of any reaction with metallic sodium also indicates that it cannot be present as an -SH group.

* Present address : Department of Chemistry, Rajshahi University, East Pakistan.

Owing probably to excessive degradation, no clear cut product could be isolated from potash fusion.

FIG. 1



Therefore, out of the whole molecule, the structure of only C_4H_6-portion and its relationship with the rest of the molecule remain to be established. Further work is in progess.

EXPERIMENTAL

Determination of Molecular Formula.—Microanalyses of the compound were carried out by Drs. Weiler and Strauss, Oxford, England, as well as by Galbraith Microanalytical Laboratory, Knoxvile, Tenn. U.S.A. (Found: C, 81.44, 81.45; H, 5.5, 5.67; S, 8.8, 8.52; M.W. 380). These values are in good agreement with the formula $C_{51}H_{12}O_2S_2$, which requires C, 81.50; H, 5.64; S, 8.53% and M.W., 751. So the formula that is accepted as the most probable one is $C_{25}H_{21}OS$ which requires C, 81.38; H, 5.69; S, 8.62% and M.W. 371.

Test for the presence of Carbonyl Group.—The substance (0.1 g.), semicarbazide hydrochloride (0.1 g.), sodium acetate (0.1 g.) and alcohol (10 c.c.) were refluxed together for 1 hour in a water-bath and then the solution was concentrated, cooled and poured into a large volume of water, when a precipitate appeared, which was washed with water, dried and crystallised from spirit, m.p. 215°. (Found: N, 9.3; S, 7.38. $C_{26}H_{24}ON_3S$ requires N, 9.8; S, 7.47%). Similarly a 2:4-dinitrophenylhydrazone, m.p. 210°, a phenylhydrazone, m.p. 120°, and an oxime, m.p. 63°, were obtained.

Attempted Preparation of a Dimedone Derivative.—To the substance (0.1 g.), dissolved in hot ethanol (20 c.c.), dimedone (0.49 g.) was added and the mixture was refluxed for 15 minutes. Water was added dropwise and the mixture was cooled when a precipitate appeared. It was filtered, washed with water and alcohol, and dried; yield 0.098 g., m.p. 153° (mixed m.p. with the original sample showed no depression).

Oxidation with $KMnO_4$.—The substance (0.37 g., 0.001 *M*) was refluxed for 2 hours with acetone (50 c.c.) containing $KMnO_4$ (2 g.). After distilling off the acetone, the residue was taken up with water. On acidification with H_2SO_4, SO_2 gas was passed till the liquid was almost clear. It was then extracted with ether

(continuous extraction). White crystals appeared on evaporating off the ether; yield 0.32 g., m.p. 121° (mixed m.p. with an authentic sample of benzoic acid showed no depression). (Theoretical amount for three moles of benzoic acid for every mole of the substance is 0.36 g.).

Reduction by Clemmensen's Method.—Zinc (12 g.) was amalgamated with $HgCl_2$ (1.2 g.), water (15 c.c.) and HCl (conc., 2 c.c.) and the mother-liquor was taken off. The substance (0.37 g.), ethanol (50 c.c) and HCl (conc., 25 c.c.) were then added to this amalgam and refluxed for 10 hours, during which more HCl (conc. 25 c.c.) was added in small portions. Alcohol was then evaporated off and the residual liquid was decanted. The solid and liquid portions were extracted with ether separately and the two ether extracts were taken together, washed with water and then dried with $CaCl_2$. On evaporating off the ether, a solid residue (0.325 g.) remained behind which could not be crystallised, m.p. 69°. It gave positive test for sulphur but no test for any carbonyl group.

Reaction with H_2O_2.—The compound (0.37 g., 0.001 *M*) was dissolved in 1 : 1 mixture of acetic acid and acetic anhydride (50 c. c.). The solution was then ice-cooled and 10 c.c. of 30% H_2O_2 (100 vol.) was added. The mixture was brought to the room temperature and allowed to stand for 3 days. White crystals that accumulated at the bottom were separated, washed with water several times and dried. Though this product melted on slow heating and ultimately disappeared completely, attempts to test for the presence of sulphur in the compound by fusion with sodium failed, because violent explosions took place. Attempts are, however, being continued.

CHEMISTRY, DEPARTMENT,
DACCA UNIVERSITY, RAMNA,
DACCA, E. PAKISTAN.

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ACID POLYMERISATION OF FURFURAL AND 5-HYDROXYMETHYL-FURFURAL

By M. V. Natesan, Premamoy Ghosh and P. K. Choudhury

The polymerisation of furfural and 5-hydroxymethylfurfural (HMF) in presence of mineral and organic acids has been studied mainly by means of light scattering and viscometry. A linear polymer has been isolated from phosphoric acid-catalysed furfural solution.

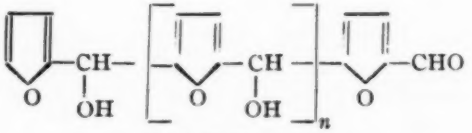
Furfural and 5-hydroxymethylfurfural (HMF) are very reactive substances. The former is obtained from hemicellulose, rich in pentosans (e.g. Oathulls), by acid hydrolysis, mainly sulphuric. The latter is obtained from cellulose via glucose.

(*a*) Hemicellulose → Pentosans $\xrightarrow[H_2SO_4]{Acid}$ Pentoses ($C_5H_{10}O_5$) (Xylose, arabinose etc.) $\xrightarrow[Acid]{-3H_2O}$ Furfural

Furfural $\xrightarrow{Acid}$ Furfural polymer.

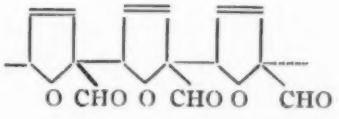
(*b*) Cellulose $\xrightarrow[H_2SO_4]{Acid}$ Glucose ($C_6H_{12}O_6$) $\xrightarrow[Acid]{-3H_2O}$ 5-Hydroxymethylfurfural

5-Hydroxymethylfurfural $\xrightarrow{Acid}$ HMF polymer.



Poly-aldolisation

(IA)



Poly-addition

(IB)

Due to the presence of a conjugated double bond (f=4) and a functional CHO group (f=1 ; total f=5) furfural can undergo both polycondensation and/or poly-addition (IA) and (IB). HMF contains one additional functional group $-CH_2OH$ and is thus more reactive than furfural (f=6). This reactivity of furfural is reflected in the ready polymerisation of furfural, either alone or in combination with phenol, aniline, urea etc. to yield a variety of highpolymers, both soluble and insoluble. With phenol it gives rise to a commercially useful phenoplastic, known as "Durite". Furfural alone furnishes a valuable plastic, known as "carbate" (carbon stock impregnated with furfural polymer). HMF polymer has not yet been commercially utilised.

Owing to the existence of (*a*) unsaturation, (*b*) conjugation of unsaturation, (*c*) reactive aldehyde group, (*d*) relatively labile 5-membered furan ring and (*e*) pseudo-aromatic properties, the polymerisation process of furfural and HMF is extremely complex, and very few theoretical studies of systematic nature have been undertaken.

The greatest obstacle for any systematic theoretical study in the acid polymerisation of furfural has been the quick cross-linking of the linear polymer, resulting in black infusible particles.

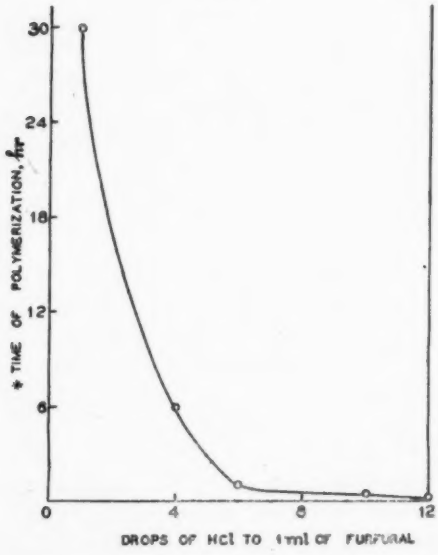
The present work was undertaken to study the mechanism of polymerisation of furfural and 5-hydroxymethylfurfural (HMF) in presence of acids, e.g., HCl, acetic and orthophosphoric acid, and to isolate the linear polymer just before gelation.

EXPERIMENTAL

(*i*). HCl-*Catalysed Polymerisation of Furfural at* 25°.—For the sake of convenience, the rate of polymerisation was qualitatively studied, by noting the time required for precipitation of the polymer as solid particles.

Freshly distilled furfural (1 c.c.) was transferred through a 1 c.c. pipette to 12 test tubes of equal capacity. Reagent HCl was then added dropwise to each test tube, 1 drop to the first tube, 2 to 2nd and finally 12 drops to the last one. The time of precipitation, indicated by the deposition of solid particles on the walls of the test tube on shaking, was recorded. This "time" was then plotted against "number of drops of HCl added to 1 c c. of furfural" to find out the convenient rate (Fig. 1). The most convenient rate for our purpose was observed to be 4 drops for 1 c.c. of furfural, the time required for precipitation of solid polymer being 6 hours.

FIG. 1



HCl-catalysed polymerisation of furfural at 25°.

The solid polymer particles were, however, found to be infusible and insoluble in the usual organic solvents. It was not possible to arrest the reaction at an intermediate linear stage. If it was stopped before the appearance of solid particles, the resultant product appeared to be almost unchanged furfural (slight polymerisation, if any, could not be detected qualitatively).

(*ii*). *Acetic Acid catalysed Polymerisation.*—With acetic acid the rate of polymerisation was too slow (no solid particles appeared even after 7 days). The colour of the solution also did not change much from the original yellow. (No black colour, only deep brown with time). This was therefore abandoned.

(iii) Phosphoric Acid-catalysed Polymerisation.—Preliminary qualitative tests with this acid showed that the reaction was much faster than with acetic acid, but slower than with HCl. Black colour developed early, but unlike HCl-catalysed reaction, the polymerisation did not proceed so rapidly as to form solid cross-linked polymers at an inconveniently fast rate. The rate of polymerisation could be easily controlled as it depended greatly on temperature. If allowed to proceed, the whole mass gradually became viscous without the separation of solid particles. The polymerisation was homogenous up to the point of gelation when solid cross-linked polymers appeared.

The course of polymerisation of furfural and HMF in phosphoric acid was studied by measurements of (*i*) light scattering and (*ii*) viscosity. An increase or decrease in turbidity or intrinsic viscosity shows polymer growth or decay. The former is more important and advantageous because unlike intrinsic viscosity, turbidity is not affected by the shape of the polymer molecule. It is much more sensitive than viscosity and is capable of detecting minute increase in the growth of the polymer.

Light Scattering

Furfural used was of Fisher's analytical reagent, twice distilled and the distillate collected at 161-62° having a light yellow colour. 5-Hydroxymethylfurfural was prepared from sucrose and purified by the method of Haworth and Jones (*J. Chem. Soc.*, 1944, 667).

The pure material distilled at 110°/0.02 mm as a light yellow mobile liquid, crystallising immediately at 0° (m.p. 31.5°). Phosphoric acid used was of Mallickrodt's analytical reagent.

The methods and the instruments used were the same as have been described previously (*J. Polymer Sci.*, 1956, **20**, 218). Reaction was carried out at 30° (± 0.1°) in a thermostatic bath.

Solutions of furfural and HMF, prepared in as short a time as possible (~ 4 hrs.) at room temperature (20-25°), were centrifuged for 1 hour at 10,000 r.p.m. and air-bubbles removed by applying vacuum for a few minutes. The solutions were kept in square light-scattering cells at 30° and intensity of laterally scattered light (I_{90}) and of transmitted light (I_0) were measured at intervals. The wavelengths of the incident beams were 436 and 546 mμ respectively. Fluorescent light was eliminated by putting another monochromatiser (interference filter) in front of the photo-multiplier. Fluorescent intensities were measured separately by replacing the interference filters by cut-off filters (Filter No. 3384 for 436 mμ and Filter No. 2424 for 546 mμ, Corning glass works, New York). Depolarisation of both scattered and fluorescent light was measured. In some cases, dissymmetries (I_{45}/I_{135}) were also determined with the Brice Phoenix light-scattering photometer. In all cases the value of I_{90}/I_0 for the solvent was subtracted from the observed value. It was found to be 0.42 for blue incident beam and 0.08 for the green beam.

The bulk of the measurements, e.g., fluorescence intensity, scattering due to the polymer, depolarisation etc. was carried out with 546 mμ as this caused less fluorescence and gave better results.

Light-scattering data of furfural and HMF in 85% phosphoric acid solution are shown in Figs. 2 and 3. The plots in Fig. 2 were obtained with blue incident beam (436 mμ). They represent the total scattering of the solutions without eliminating fluorescence. As fluorescent light cannot be satisfactorily eliminated at this wavelength (436 mμ) even with an additional monochromatiser (interference filter), fluorescence was not measured in this case.

FIG. 2

Conc. = 0.108 g./100 c.c.
At 436 mμ.

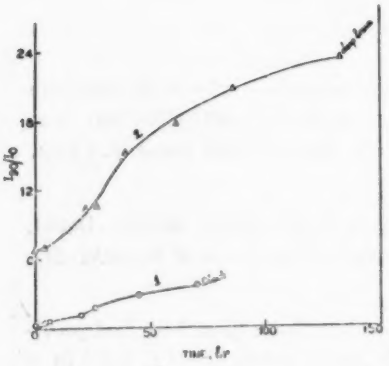
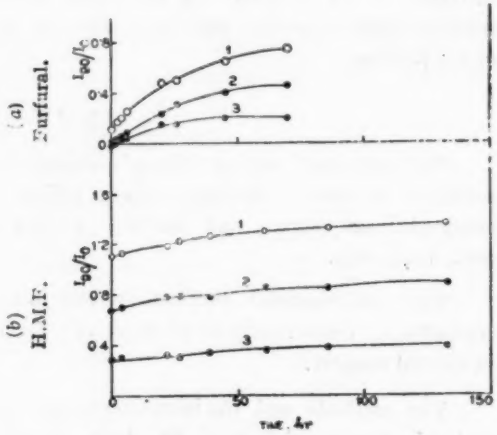


FIG. 3

At 546 mμ.



1. Without filter.
2. With monochromatic filter.
3. With cut off filter.

The plots show increasing I_{90}/I_0 value, but in the case of furfural, measurements could not be conducted beyond 70 hours as the solution turned black. Initially, the solution was light yellow, but it gradually turned darker, till after 70 hours, no measurement was possible, although the concentration was as low as 0.108 g./100 c.c. With higher concentrations, the solution turned black much earlier.

In the case of HMF, the solution was initially light brown in colour which grew deeper with time, but at no time it was as dark as that of furfural. As satisfactory measurements were made possible with this concentration (0.026 g./100 c.c.), higher concentrations were not attempted.

The higher I_{90}/I_0 value at the initial stage (0 hr.) for HMF may be due to the fact that HMF produced by the Haworth method in the laboratory could not be made absolutely pure and might contain some polymerised material, which accounted for the higher initial value. (Incidentally this shows the higher reactivity

of HMF). This is also supported by the fact that furfural, which was twice distilled before use, gave almost the theoretical value (zero value at 0 hr), under identical conditions.

The plots in Figs. 3(*a*) and 3(*b*), obtained with green incident beam (546 mμ), show clearly that polymers from furfural and HMF are being produced in phosphoric acid solutions. That fluorescence has been elimiuated to a very great extent is shown by the lower values in curve 3 in Fig. 3(*a*) and (*b*). Low depolarisation values (0.30-0.55) also confirm that the fluorescence intensity is small. Curve 2 in the same figure is essentially due to the growth of the polymers from furfural and HMF (I_{90}/I_0 of curve 1 cannot be compared directly with that of curve 3 because of the dependence of the photo-multiplier sensitivity on wave-length).

No increase in viscosity with this concentration of furfural (0.108 g./100 c.c. and HMF (0.026 g./100 c.c.) in 85% H_3PO_4 could be detected although the viscosity measurements for the two were continued for over 100 hours.

Viscometry

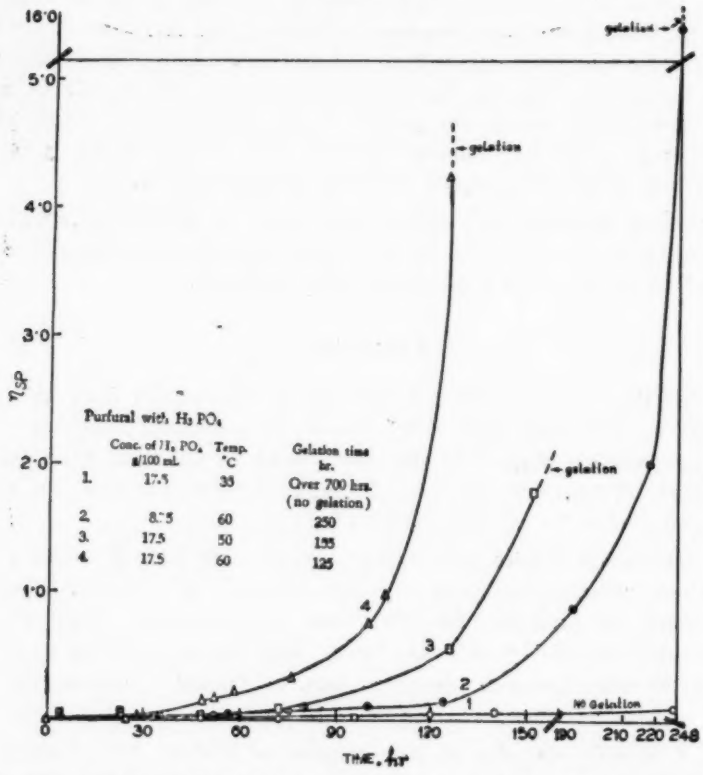
It was felt that if the linear polymer had to be isolated from the solution, the concentration of furfural and HMF should be considerably increased and the course of polymerisation studied to the point, short of gelation, when the reaction could be arrested. Viscometry, which is unaffected by changes in colour formation, was therefore adopted as the means for this study.

Several viscometric studies with furfural were made with H_3PO_4, the concentration of which varying from 9 to 18 g. per 100 c.c. of furfural. Temperature was also varied to ascertain its effect on polymerisation. Three thermostatic baths at 35°, 50° and 60°(±0.1°) were used. Readings were taken in the Ostwald type viscometers with flow-time over 100 secs. at regular intervals till gelation occurred.

In Fig. 4, specific viscosity of four samples of furfural with different concentrations of H_3PO_4 and at different reaction temperatures has been plotted against time to show the increase in viscosity with the progress of polymerisation. Low temperature does not help polymerisation as is shown by curve 1 in Fig. 4, where the increase in viscosity is regular but small. With 17.5% H_3PO_4, the gelation does not take place even after 700 hours although there is a gradual increase. That the reaction is temperature-dependent is shown very effectively by curves 3 and 4. At 50° with the same concentration of H_3PO_4, gelation takes place after 155 hours (curve 3) whereas with the same concentration at 60°, the gelation time is reduced to 125 hours only (curve 4). Lowering of the concentration to half of its original (8.75%) value prolongs the time of gelation to 250 hours, the nature of the curve remaining the same. Thus the effect of H_3PO_4 and temperature on the course of polymerisation is clearly indicated. The most striking difference between the H_3PO_4-catalysed and HCl-catalysed polymerisation of furfural was that irrespective of whether the gelation stage was reached sooner or later, the polymerisation

was homogenous throughout the entire course in each case and at no stage during the prolonged polymersation process, solid cross-linked polymers separated out of furfural solution (as happened with HCl).

FIG. 4



HMF has not yet been studied viscometrically but will be taken up soon.

To isolate the linear polymer, the reaction was arrested just before gelation, when the solution became a very viscous jelly-like mass. This was partially soluble in alcohol but was completely soluble in acetone. It contained a very small amount of unchanged furfural and could be moulded after being compounded with suitable fillers. The unchanged furfural acted as plasticizer and did not interfere with the moulding process. The end-product was a useful thermosetting material and was observed to be unaffected by high temperature, organic solvents, chemical reagents and moisture.

APPLIED CHEMISTRY DEPARTMENT,
UNIVERSITY OF CALCUTTA,
CALCUTTA-9

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BROMINATION OF ARYLAMIDES OF 4-METHOXYBENZOIC ACID

By D. M. Phatak and G. V. Jadhav †

Bromination of arylamides of 4-methoxybenzoic acid under different conditions has been effected and the constitution of the bromo derivatives determined.

The present investigation is the continuation of the work of one of the authors (G.V.J.) on the effect of methylation of the hydroxy group of 4-hydroxybenzoic acid. Jadhav and Nerlekar (*J. Univ. Bombay*, 1951, **20**, III, 97; this *Journal*, 1952, **29**, 234) found that the introduction of the negative group like $-NO_2$ had practically no effect on the reactivity of the two nuclei towards bromination. The same authors (this *Journal*, 1952, **29**, 765) found, however, the acidic nucleus to have been completely deactivated by methylating the hydroxy group in the case of 2-hydroxy-5-nitrobenzoic acid, as bromo derivatives with bromine in the nucleus containing amino group were obtained.

It has been found now that bromine enters the basic part, when bromination is carried out in acetic acid medium, except in the case of *o*-nitroanilide, when it is found to be present in the acidic part, which is probably due to the deactivation of the basic nucleus by the $-NO_2$ group. With liquid bromine, higher bromo derivatives with bromine in the acidic part also are obtained.

The constitution of the bromo derivatives is arrived at by hydrolysing them with 80% (v/v) sulphuric acid and identifying the acidic and the basic components by mixed melting point with the authentic specimens.

Experimental

Bromination in Acetic Acid Medium.—To the arylamide (1 g.), dissolved in hot acetic acid (20 c.c.), 30% (w/v) solution of bromine in acetic acid was added and the reaction mixture was allowed to cool slowly. The solid which separated was filtered and crystallised from a suitable solvent, yield 0.7-0.8 g. in each case. The results are described in Table I.

Table I

[B represents 4-methoxybenz-]

Arylamides.	30% Br_2 added.	Bromo derivative.	Cryst. from.	Cryst shape.	M.P.	Mol. formula.	% Bromine Found.	% Bromine Calc.
* B-anilide	7.0 c.c.	B-4′-bromo-anilide	Acetic acid	Colorless needles	214-15°	$C_{14}H_{12}O_2NBr$	26.3	26.1
B-*m*-toluidide	6.7	B-4′-bromo-*m*-toluidide	Dilute acetic acid	Do	154-55°	$C_{15}H_{14}O_2NBr$	25.4	25.0
** B-*p*-toluidide	6.7	B-2′-bromo-*p*-toluidide	Alcohol	Do	135-36°	,,	25.2	25.0
B-*o*-nitroanilide	5.7	3-Bromo-B-*o*-nitroanilide	Benzene	Yellow needles	172-73°	$C_{14}H_{11}O_4N_2Br$	22.5	22.8
B-*β*-naphthyl-amide	5.7	B-α-bromo-*β*-naphthylamide	Alcohol	Colorless needles	169-70°	$C_{18}H_{14}O_2NBr$	22.6	22.5

† Present address : D. E. Society's Bombay College, Bombay-28.
* The constitution has also been proved by synthesis.
** The basic component obtained in hydrolysis is characterised through the hydrochloride.

Bromination with Liquid Bromine.—The arylamide (1 g.) was gradually added to liquid bromine (2 c.c.) when it went into solution. The reaction was allowed to proceed at room temperature for a day or two. The reaction mixture was diluted with water. The solid obtained was triturated with sodium bisulphite solution and crystallised from a suitable solvent. The yield of the bromo derivative was about 1.2 g. in all cases. The results are described in Table II.

TABLE II

[B represents 4-methoxybenz-, and
B_1 represents 3-bromo-4-methoxybenz-].

Arylamides.	Bromo derivative.	Cryst. from.	Crvst. shape	M.P.	Mol. formula.	% Bromine Found.	% Bromine Calc.
B-anilide	B_1-2′; 4′-dibromo-anilide	Acetic acid	Colorless needles	185-86°	$C_{14}H_{10}O_2NBr_3$	52.0	51.7
B-*m*-toluidide	B_1-4′ : 6′-dibromo-*m*-toluidide	Alcohol	Soft Do	157-58°	$C_{15}H_{12}O_2NBr_3$	50.5	50.2
B-*p*-toluidide	B_1-2′: 5-(or 3′ : 6′)-dibromo-*p*-toluidide	Acetic acid	Do	195-96°	,,	50.0	50.2
B-*o*-anisidide	B_1-5′ : 6′-dibromo-*o*-anisidide	,,	Do	224-25°	$C_{15}H_{12}O_3NBr_3$	48.7	48.6
B-*p*-anisidide	B_1-2′ : 5′-(or 3′ : 6′)-dibromo-*p*-anisidide	,,	Colorless wooly needles	230-31°	,,	49.0	48 6
B-β-naphthyl-amide	B_1-1′ : 3′ : 6′-tribromo-β-naphthylamide	Nitro-benzene	Colorless needles	262-63°	$C_{18}H_{11}O_2NBr_4$	53.6	53.9

Hydrolysis.—The bromo derivative (1 g.) was heated with 80% H_2SO_4 (20 c.c.) on a boiling water-bath for about 6 hours. The solid separating on dilution was filtered and washed and then treated with sodium bicarbonate solution, when the unhydrolysed substance remained insoluble and the acid went into solution. On acidifying the filtrate the acid was obtained. It was characterised by mixed melting point with an authentic specimen.

The first acidic filtrate on neutralisation gave the basic component which was purified and identified by mixed melting point with authentic specimens.

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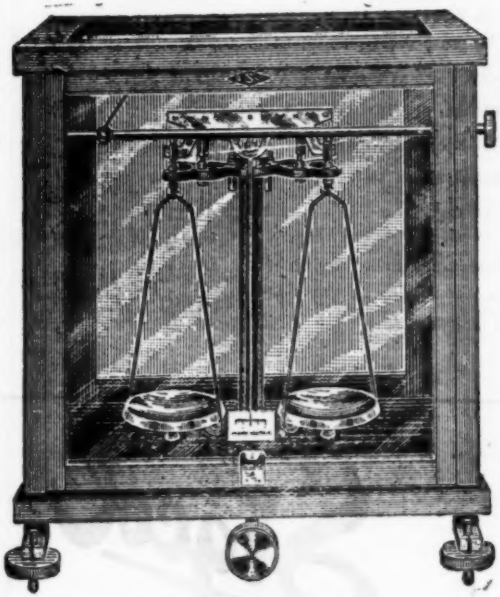

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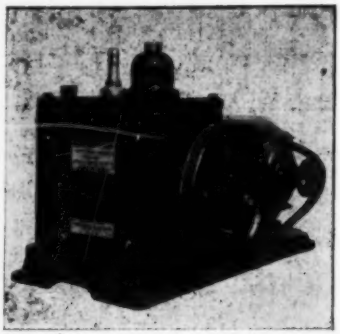

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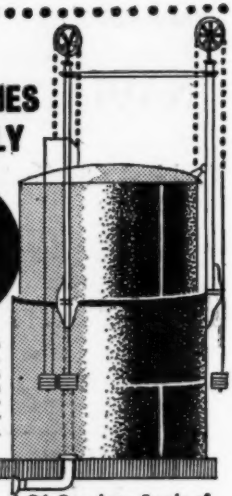

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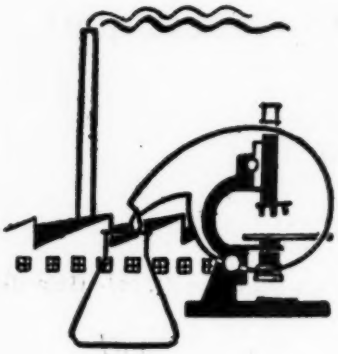

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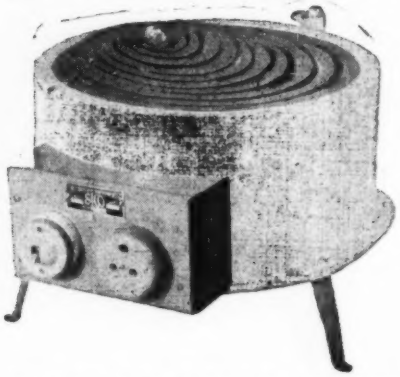

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